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Volume V . . . . . PHYSICAL

The latter four are in course of preparation

A TEXTBOOK

of

INORGANIC CHEMISTRY

by

R. E. W. SOMMER, Ph.G.

Dean of the Pharmaceutical Department
and Professor of Chemistry
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MILWAUKEE
HERBERT HAYWARD
1906

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PREFACE

THAT THERE MAY BE no misconception of this work, the author wishes it to be understood that it is in no sense intended as an exhaustive treatise on the subject of Inorganic Chemistry, but rather as an easily-understood book for those who enter upon the study of Chemistry without the proper preliminary training in physico-chemical facts and their philosophy. Realising that a too-scientific treatment offers a stumbling-block to many students, effort has been made to present the various subjects in as simple a manner as is compatible with correctness. In the earlier part of the work, familiar names—as Epsom salt, blue vitrol, etc.—have been employed; while later the exact chemical nomenclature has been adhered to.

As the work is especially intended for Pharmaceutical, Medical and Dental Students, the inorganic chemicals of the United States Pharmacopoeia are listed, together with their preparations. These, however, are dealt of but briefly, and it is hoped that the book may be of value in other fields of chemical endeavor.

Objections may be raised to the lengthy explanations of apparently self-evident facts, the repetitions, and other faults of like nature: the author is keenly alive to these deficiencies, but believes they are excusable if they emphasize the facts it is desired to convey.

To the possible criticism that certain subjects are superficially treated, we repeat that the work is intended for beginners; and if the work stimulate even a few students to a deeper knowledge of this vast subject, the author will be more than repaid.

Milwaukee, Wis.,
Aug. 18, 1906.

RICHARD E. W. SOMMER.

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Part I

GENERAL CHEMISTRY

CHAPTER I.

ESSENTIAL DEFINITIONS, PROPERTIES OF MATTER, ETC.

A BODY is a part of space. Like space it has three dimensions, length, width and height.

Measurement of the dimensions is made in standard terms, of which the meter is the base. This is the international unit, and is equal to one forty-millionth of the earth's circumference around the poles. The larger denominations are multiples of the meter by 10, 100 and 1000; and are designated by the greek prefixes deka-, hekto- and kilo- respectively. The smaller denominations are one-tenth, one-hundredth and one-thousandth of the meter and have the latin prefixes deci-, centi- and milli- respectively.

One-thousandth meter—One Millimeter.
One-hundredth meter—One Centimeter.
One-tenth meter—One Decimeter.
UNIT—ONE METER.
Ten meters—One Dekameter.
One hundred meters—One Hektometer.
One thousand meters—One Kilometer.

Measurement of surface is expressed in terms which are squares of the linear measurements.

VOLUME is the quantity of space occupied by a body.
Measurement of volume is expressed in terms which are cubes

of the linear measurements—Cubic centimeters, cubic decimeters, etc. The *liter* is the unit for measuring liquids, and is equal to a cubic decimeter. The larger and smaller denominations have the same prefixes as the corresponding ones of the meter.

SHAPE is the contour of a body as determined by its borders.

MATTER is that which occupies space. It is perceived by the senses, directly or indirectly. Air is matter, although it cannot be directly recognised by the senses, as it is a colorless, odorless tasteless gas. It can be *indirectly* recognised, however, by the fact that water cannot be introduced into a bottle containing air without the air being first expelled..

BODIES may be classified as

Mathematical or *geometrical,* possessing only volume and shape. These do not contain matter, and, as they are not perceived by the senses, can only be speculated upon: and

Physical or *real,* which have volume and shape and consist of matter. They are, therefore, perceived by the senses.

NATURE is the totality of all real bodies—animals, plants, minerals, heavenly bodies, etc., etc.

A SCIENCE is a systematic and orderly arrangement of knowledge.

NATURAL SCIENCES are systematic and orderly arrangements of the knowledge of real bodies. There are two distinct classes:

Descriptive natural sciences, which merely describe the sense-impressions obtained from real bodies—to these belong Zoology, Botany, Minerology, etc.; and

Exact natural sciences, which investigate the changes undergone by real bodies and try to ascertain the causes of such changes. This class includes Chemistry, Physics, Physiology, etc.

Knowledge of real bodies can be obtained by observation and by experimentation.

EXPERIMENTATION is the placing of a substance under

artificial conditions in order to note its behavior in this environment.

OBSERVATION is the study of those phenomena which occur *without* the interference of the observer.

EXPERIENCE is the accumulated knowledge obtained by observation and experiment, and is therefore the total knowledge obtained through the senses.

EMPIRICAL KNOWLEDGE is that which is only obtained through the senses. As all knowledge in the natural sciences is gotten either by observation or experimentation, they are sometimes called *empirical sciences.*

AN HYPOTHESIS is a supposition brought forward to explain facts, and is therefore only an imagination and not necessarily a truth. It may be discarded if it prove to conflict with later observations and experiments.

A THEORY is a development of an hypothesis which has been substantiated by a certain amount of empirical knowledge. It is borne out by so many facts that it not only stands the test of experience, but is also not inconsistent with other known facts.

A NATURAL LAW is a theory which is affirmed by so great a number of facts that we may consider it as a general truth; or according to Huxley, as a rule that we have always found to hold good and always expect will hold good.

The chemist makes two principal divisions of matter, viz.:

COMPOUND SUBSTANCES—those which can be separated into two or more entirely different materials by any known method (heat, light, electricity, etc.); and

SIMPLE SUBSTANCES or CHEMICAL ELEMENTS—those which all known methods fail to further separate.

Examples of compounds are water, which can be split up into Oxygen and Hydrogen; salt, which can be split up into Sodium a silver-like metal and Chlorine, a greenish gas; etc. Examples

of elements are Hydrogen, Sodium, Chlorine: these cannot, as yet, be further separated.

It will be seen that this classification of elements depends upon the present methods of separating substances into simpler components. It is possible that in the future these methods will be so much improved that substances now regarded as elements may be then split up into simpler components and cease to be so classed.

The class of compounds is very numerous, hundreds of thousands of them being known. In addition, new ones are being constantly prepared.

The class of elements is relatively small. It is impossible to give a definite number, because:

(a) New elements continue to be discovered; and

(b) It may be possible to split up in the future substances now regarded as elements. This has been the case with many substances—quicklime was for a long time considered to be an element, but was later found to consist of Calcium and Oxygen.

(c). It is doubtful whether some substances should be classed as elements or compounds.

Approximately there are about 80 elements. The following table gives a list of them.

TABLE OF ELEMENTS.

NAME	SYMBOL.	VALENCE.	ATOMIC WT.
Aluminum	Al.	3	26.9
Antimony	Sb.	3, 5	119.3
Argon	A		39.6
Arsenic	As.	3,5	74.4
Barium	Ba.	2	136.4
Bismuth	Bi.	3, (5)	206.9
Boron	B.	3	10.9
Bromine	Br.	1	79.36
		With Oxygen, 1, 3, 5, 7.	
Cadmium	Cd.	2	111.6
Caesium	Cs.	1	131.9
Calcium	Ca.	2	39.7

NAME	SYMBOL.	VALENCE.	ATOMIC WT.
Carbon	C.	4	11.91
Cerium	Ce.	3 (also 4)	139.2
Chlorine	Cl.	1	35.18
		With Oxygen, 1, 3, 5, 7.	
Chromium	Cr.	(2) 3, 6	51.7
Cobalt	Co.	2, (3)	58.55
Columbium	Cb.	3, 5	93.3
Copper	Cu.	(1), 2	63.1
Erbium	Er.	3	164.8
Fluorine	F.	1	18.9
Gadolinium	Gd.	3	154.8
Gallium	Ga.	3	69.5
Germanium	Ge.	2, 4	72.
Glucinium	Gl.	2	9.03
Gold	Au.	(1), 3	195.7
Helium	He.		4.
Hydrogen	H.	1	1.
Indium	In.	3	114.1
Iodine	I.	1	126.01
		With Oxygen, 1, 3, 5, 7.	
Iridium	Ir.	2, 4	191.5
Iron	Fe.	2, 3, (6)	55.5
Krypton	Kr.		81. 2
Lanthanum	La.	3	137.9
Lead	Pb.	2, (4)	205.35
Lithium	Li.	1	6.98
Magnesium	Mg.	2	24.18
Manganese	Mn.	2, (3, 6, 7)	54.6
Mercury	Hg.	1, 2	198.5
Molybdenum	Mo.	2, 4, 6	95.3
Neodymium	Nd.	3	142.5
Neon	Ne.		19.9
Nickel	Ni.	2, (3)	58.3
Nitrogen	N.	(1), 3, 5	13.93
Osmium	Os.	2, 4	189.6
Oxygen	O.	2	15.88
Palladium	Pd	2, 4	105.7
Phosphorus	P.	(1), 3, 5	30.77
Platinum	Pt.	(2), 4	193.3
Potassium	K.	1	38.85

NAME	SYMBOL.	VALENCE.	ATOMIC WT.
Praseodymium	Pr.	3	139.4
Radium	Ra.	2	223.3
Rhodium.	Rh.	2, 4	102.2
Rubidium	Rb.	1	84.9
Ruthenium	Ru.	2, 4	100.9
Samarium	Sm.	3	149.2
Scandium	Sc.	3	43.8
Selenium	Se.	2	78.6
		With Oxygen. 2. 4. 6.	
Silicon	Si.	4	28.2
Silver	Ag.	1	107.11
Sodium	Na.	1	22.88
Strontium	Sr.	2	86.94
Sulphur	S.	2	31.83
		With Oxygen, 2. 4. 6.	
Tantalium	Ta.	3, 5	181.6
Tellurium	Te	2	126.6
		With Oxygen, 2, 4, 6.	
Terbium	Tb.	3	158.8
Thallium	Tl.	1, 3	202.6
Thorium	Th.	4	230.8
Thulium	Tu.	3	169.7
Tin	Sn.	2, 4	118.1
Titanium	Ti.	4,	47.7
Tungsten	W.	2	182.6
		With Oxygen. 2, 4, 6	
Uranium	U.	4, 6	237.7
Vanadium	V.	3,5	50.8
Xenon	Xe.		127.
Ytterbium	Yt.	3	171.7
Yttrium	Yt.	3	88.3
Zinc	Zn.	2	64.9
Zirconium	Zr.	4	88.9

The following elements have synonyms:

Antimony . . .	Stibium	Mercury .	Hydrargyrum
Columbium . .	Niobium	Potassium . .	Kalium
Copper	Cuprum	Silver	Argentum
Glucinium . .	Beryllium	Sodium . . .	Natrium
Gold . . . r .	Aurum	Tin	Stannum
Iron	Ferrum	Tungsten . .	Wolfram
Lead	Plumbum		

Valences in parenthesis are rare.

COMPOSITION of a body is the quantity, quality and arrangement of the elements it contains. Changes suffered by a body may be either

1. *Physical*—those which do not affect the composition of the body. A substance which has undergone a physical change remains unaltered in its essence and can be easily recognised as the same substance. The magnetisation of steel needles,, the expansion of Mercury in a thermometer and the melting of Lead are physical changes.

2. *Chemical*—those which affect the composition of a body. A substance suffering a chemical change is so altered in its essence that it loses its identity, and the original substance can seldom be recognised in the products formed. The burning of wood, the dissolving of a metal in an acid and the explosion of gunpowder are chemical changes. Every chemical change is attended by a physical one.

PHYSICS is the science which treats of changes not affecting the ultimate composition of substances.

CHEMISTRY is the science which treats of the composition of bodies, their changes in composition, and the laws governing such changes.

A PHYSICAL SYSTEM consists of two or more bodies which affect one the other so that a physical change takes place in them. For instance, a falling stone forms with the earth a physical system.

A CHEMICAL SYSTEM consists of two or more bodies which affect each other chemically.

The chemist has two methods for investigation:

1. ANALYSIS—The process of decomposing compounds into *simpler* compounds or elements.

(a) *Ultimate analysis*—the process of decomposing compounds into elements.

(b). *Proximate analysis*—the process of splitting compounds

into simpler compounds. An example of this is seen in milk, in which the quantities of casein, water, sugar, butter, etc., which it contains are determined. All these substances are compounds, but are more simply constructed than milk.

(c). *Qualitative analysis*—the process of decomposing compounds in order to find out the *quality* and not the quantity of the simpler constituents.

(d). *Quantitative analysis*—the process of decomposing compounds in order to find out the *quantities* of the simpler constituents.

2. SYNTHESIS—The process of building up compounds from elements (*ultimate synthesis*), or from simpler compounds (*partial synthesis*).

Elements are often divided into

1. METALS: These are solids at ordinary temperatures (except Mercury, which is a fluid) and are opaque, their smooth surfaces reflecting light and giving them the so-called metallic lustre. They are good conductors of heat and electricity. This is the more numerous class, about 55 to 60 elements being metals.

2. NON-METALS: Some of these are gases, like Oxygen, Hydrogen, Nitrogen, Chlorine and the Argon class; and others are solids, like Sulphur, Phosphorus, Carbon, etc. One, Bromine, is a liquid. They are not good conductors of heat or electricity, and are characterised by an absence of the properties possessed by the metals. This is the smaller class, but may be regarded as the more important for the student because the knowledge of them is more important to the understanding of Chemistry.

As these two classes gradually merge into each other, certain elements are sometimes placed in one division and sometimes in the other. These elements, which have some of the properties of both metals and non-metals, are called *amphoteric* elements or *metalloids*. Antimony and Arsenic are metalloids.

Another classification of elements will be given later (*see periodic law*).

COMPOUNDS may be classified into *chemical compounds* and *mechanical mixtures.* A chemical compound differs from a mechanical mixture in the following properties:

(a) Its component parts are so altered by their union that it is impossible to recognise them by the senses or separate them by methods other than chemical ones; while in a mechanical mixture the simple constituents are not altered and can be recognised by the senses or separated by methods which are not chemical ones. Blue vitrol is an example of a *chemical* compound. In it we cannot recognise the yellow Sulphur, the red metallic Copper and the gaseous Oxygen which it contains.

An example of a physical mixture is that of Iron-powder and Sulphur-powder, greyish-white in color, in which it is easy to identify the two constituents with the aid of a magnifying-glass; they can also be separated by dissolving the Sulphur in Carbon disulphide, which will not dissolve the Iron, or by a magnet, which will attract the Iron but not the Sulphur.

(b) In chemical compounds the weight-quantities of the elements contained have certain definite proportions, while a mechanical mixture has any varying proportions that may please the mixer. For instance, in order to prepare the chemical compound Potassium-iodide, it is necessary to take weight-quantities of the two elements in the ratio of 39:126; while in order to prepare a mechanical mixture of Iron and Sulphur powders any weight-proportions may be used. This law of ratio in chemical compounds is very important. (*see law of definite proportions*).

(c). When a chemical compound is formed, the temperature of the system is invariably altered—in most cases an increase being noted. It may be so marked that light is produced and even explosions occur. Electrical processes often accompany chemical processes. Such thermal, optical and electrical phenomena are not seen when a simple mechanical mixture is made.

THE WEIGHT-LAWS OF CHEMISTRY.

1. *Law of the indestructibilty of matter.* During all possible changes, physical or chemical, which a system of bodies may undergo, one property is always permanent—the weight (or more

properly, the mass). If we melt Lead, the molten will weigh just as much as the solid Lead did. Should we evaporate water, the resultant steam has exactly the same weight as the water had. Whether a body be expanded by heat, magnetised, electrified or whatever may happen to it, its weight does not change. When Iron rusts, the rust contains just as much Iron as was originally in the form of the pure metal. If Silver be dissolved in nitric acid, the Silver-nitrate obtained contains just as much Silver as was taken. This law of the indestructibility of matter and the law of the conservation of energy are the most important natural laws; they limit the power of man, who can neither create nor destroy but can only make different arrangements in a given system of bodies and cannot change the total quantity of matter or energy which a system contains, except at the expense of another system.

2. *The law of the constant or definite proportions* (*discovered by Richter*). Every pure chemical compound has a certain unchangeable quantitative composition, regardless of the manner of its origin or preparation. Pure water can be obtained by distilling rain-water, well-water, spring-water, plant-juices, blood, by burning Hydrogen and in many other ways; but no matter from whatever source it is obtained, the pure water invariably contains the same proportions, by weight, of the two elements—that is, 9 kilograms of water contain 8 kilograms of Oxygen and 1 kilogram of Hydrogen.

3. *Law of the multiple proportions* (*discovered by Dalton*, 1808). In many instances two elements form not only one but several compounds. In such instances the weight-quantities of one of the elements which have united with a standard quantity of the other element bear the simple ratio 1:2:3:4:5.

EXAMPLE I. Hydrogen and Oxygen form two compounds,

(a) Water, containing *one* weight-part of hydrogen and *eight* weight-parts of Oxygen; and

(b) Hydrogen-peroxide, containing one weight-part of Hydrogen and *sixteen* weight-parts of Oxygen.

The quantities of Oxygen which have united with the standard

weight (one part) of Hydrogen are *eight* and *sixteen*; these have the simple ratio of 1:2.

EXAMPLE II. Nitrogen and Oxygen form five compounds. An analysis of them gives the following results:

Compound 1 contains 1 gm. N and 0.57 gm. O
Compound 2 contains 1gm. N and 1.14 = 2 x 57 gm. O
Compound 3 contains 1 gm. N and 1.71 = 3 x 57 gm. O
Compound 4 contains 1 gm. N and 2.28 = 4 x 57 gm. O
Compound 5 contains 1 gm. N and 2.85 = 5 x 57 gm. O

Hence we see that the quantities of Oxygen which have united with the standard weight of Nitrogen in these various compounds have the ratio 1:2:3:4:5.

The combining weight of an element is the smallest weight-part of it which will unite with one weight-part of Hydrogen. We have seen that in the two compounds of Hydrogen and Oxygen the smallest weight-part of Oxygen which unites with one weight-part of Hydrogen is eight, therefore this is its combining weight. Below are those of a few other elements.

Hydrogen, 1	Bromine, 80.
Oxygen, 8.	Chlorine 35.5.
Sulphur, 16.	

4. *Law of the reciprocal proportions* (*discovered by Wenzel,* 1774). The quantities(combining weights) in which the elements unite with one part of Hydrogen express also the relation of the quantities, or a multiple thereof, in which they unite with each other. For instance, the smallest quantity of Oxygen which unites with 1 gram of Hydrogen is 8 grams; and the smallest quantity of Chlorine which unites with 1 gram of Hydrogen is 35.5 grams. Then when Oxygen unites with Chlorine the relation between the two weight-quantities must have the ratio of 8:35.5; or it may be 2x8, 3x8, 4x8, etc., grams of Oxygen which unite with 35.5 grams of Chlorine.

The law of the reciprocal proportions makes possible a very practical extension of the definition of combining weights. According to the definition just given, combining weights can be experimentally determined by combining the element with Hydrogen, forming as many compounds as possible. These are

then subjected to quantitative analysis and the smallest weight-quantity of the element which is found in any one of the compounds is taken as the combining weight of the element. But there are many elements—all of the metals—which do not unite with Hydrogen, and therefore this is not practicable for the determination of their combining weights. Now, according to the law of the reciprocal proportions, the smallest weight-quantity of an element which unites with one weight-quantity of Hydrogen also unites with eight weight-parts of Oxygen; and, as all the elements, except Fluorine and the Argon class, easily unite with Oxygen, the combining weights of elements can be determined by analysis of their Oxygen compounds. The definition may therefore be extended as follows:

Combining weight is the smallest weight-quantity of an element which unites with 1 weight-part of Hydrogen, or 8 weight-parts Oxygen.

GENERAL PROPERTIES OF MATTER.

The general properties of matter are those properties which are invariably possessed by all real bodies. They are *Volume, Mobility, Impenetrability, Inertia, Gravitation, Indestructibility, Divisibility, Porosity, Compressibility, Elasticity and Density.*

I. EXTENSION or VOLUME or MAGNITUDE is the quantity of space occupied by a body.

II. MOBILITY. All matter is in a state of constant motion.

III. IMPENETRABILITY is the property by which two portions of matter cannot simultaneously occupy the same space. This is shown by the fact that water cannot be poured into a bottle containing air without the air being expelled.

IV. INERTIA is the incapability of matter to change its state of motion or of rest. Since rest is negative motion, and as no body is in absolute rest, we may dispense with this definition and state that inertia is the resistance which a body offers to changes in its state (direction and velocity) of motion. As a body is not of itself capable of changing its state of motion, it it is necessary to assume a cause located outside of it to account for any such change; this external cause is called *force.* Hence the definition:

FORCE is that which produces, or tends to produce, change in the state of motion of a body.

MASS of a body is the quantity of matter which it contains; or mass is the magnitude of resistance which a body offers to change of its state of motion. Masses are measured in the metric system in grams, kilograms, etc.

WORK is motion against a resistant force. Therefore work can only be performed when there is motion as well as resistant force in the system of bodies. When the steam in the cylinder of an engine presses against the piston and drives it out, there is motion against a resistant force and work is done. A team of horses, attached to a loaded wagon, perform no work in spite of their exertions, if they fail to move the wagon, because there is no motion. The planets, in their course around the sun, do not perform work because there is no force resisting their motion. They move solely by virtue of their inertia.

Measure of Work. Work (L) is the product of the resistant force (F) and the distance (d) through which the body travels.

$$L = F \times d.$$

As force, like weight (which is a force), is measured in grams, kilograms, etc., and as distance is measured in meters, it follows that

The unit of Work is that amount performed when a body having a weight of one kilogram is raised through a distance of one meter.

ENERGY is the ability to do work. There are two kinds:
Kinetic or *Actual,* also called *Energy of Motion* is possessed by any system of bodies which change their relative positions one to another. For instance, a falling body (or rather the system: falling body—earth) possesses kinetic energy because during the fall of the body it is capable of performing work. The energy of falling bodies is utilised in watermills, weight-clocks, etc.

Potential Energy or Energy of Position; that which a system of bodies at relative rest as regards each other possess by virtue of their respective positions. A wound-up watchspring possesses potential energy by reason of the relative position of its molecules to each other. When the spring is released is does work.

Another example is that of a falling stone up on the hilltop which, by virtue of its elevated position with reference to the earth, possesses potential energy. Were the support of this stone to be removed at any time, it would fall and could do work in its descent. Therefore, although in a state of relative rest, it has the inherent *capacity to perform work.*

ENERGY may be also divided into

Mechanical or *Molar Energy*—That possessed by a system of bodies in which masses larger than molecules participate. The examples of kinetic and potential energy given also illustrate mechanical energy.

Thermal or *Heat Energy* is the kinetic energy of molecules. Modern Physics teaches that heat is the vibration of molecules.

Chemical Energy is the potential energy of atoms. Substances like Nitro-glycerine, etc., possess energy by reason of the relative position of their component atoms and by the ability of these to change their relative positions and form other compounds, thus performing work.

Electrical Energy, Magnetic Energy, Optical Energy and the *Energy Emanating from Radium and Like Substances* may also be mentioned here.

The measure of energy is the work it is capable of performing.

CONVERSION OF ENERGY. Energy may be converted from one form to another. A favorite of this is the conversion of the kinetic into potential energy and vice versa in the ascent and fall of a stone. When thrown it possesses no potential but only kinetic energy—that given to it by the arm of the thrower. As it ascends it gradually loses its velocity and with this its kinetic energy, but gains in potential as its distance from the earth increases. At the highest point it reaches a state of rest and possesses, therefore, at this moment, no kinetic but its maximum potential energy. During its fall it gradually loses potential as its distance from the earth decreases, but gains kinetic energy as its velocity increases. Conversion of energy also occurs in the steam engine. The chemical energy stored up in the coal

is liberated when the fuel burns under the boiler, and is converted into heat energy, causing the water to boil. The steam formed moves the piston in the cylinder and drives the engine, thus converting the heat energy into mechanical energy. In the dynamo the mechanical enery is changed into electrical energy, and this can be conducted to an electric lamp and made to furnish optical energy (light) or by means of a motor can be restored to mechanical energy again, or passed through chemical substances and converted into chemical energy.

LAW OF THE CONVERSION OF ENERGY. The quantity of each of these energy forms can be measured by the amount of work it is capable of performing. A close examination of all phenomena by which one energy form can be converted into another shows that the totality of all energy in a certain system cannot change; no form of energy can be produced except at the expense of some other, nor annihilated except to appear in another form. This conversion occurs in certain definite proportions, and these are called the energy-equivalents. This law was first clearly recognised by Robert Mayer in his studies of the equivalents of heat and mechanical energy. It is common knowledge that heat produces mechanical energy, as seen in the case of the steam engine; and that friction, which is mechanical energy, produces heat. Exact experiments by Mayer and later by Joule and Hirn prove that one *Calory* of heat (the amount necessary to raise the temperature of one kilogram of water from zero to one degree Centigrade) invariably produces 424 kilogram-meter of work, and that 424 kilogram-meter of work produce one Calory of heat. Therefore one Calory is equal to 424 kilogram-meter of work, or one kilogram-meter is equal to 1-424 Calory.

The quantity 1-424 is usually designated in physico-chemical works by the letter A and is called *the mechanical equivalent of heat.*

Helmholz generalised the law to apply to all energy forms and since that time the various equivalents of different energy-forms—as the electrical equivalent of mechanical energy, the heat-equivalent of electricity, etc., have all been determined. They have been invariably found to substantiate the law.

If the whole universe be considered as a system of bodies, we may express the law of the conservation of energy as follows:

The total sum of Energy in the universe, like the total sum of Matter, is a constant, unvarying quantity.

V. GRAVITATION is the attraction which exists between all masses. This important law was discovered by Newton and may be stated as follows: *All bodies in Nature exert a reciprocal attraction upon each other which is proportional to their masses and inversely proportional to the square of their distance.*

As the masses of all bodies on the surface of the earth are comparatively very small, it follows that the earth attracts other terrestrial bodies much more than they do it. Bodies removed from the earth's surface fall towards it when they are not supported on account of this attraction.

WEIGHT is the measure of gravity between the earth and other terrestrial bodies; that is, the measure of the magnitude of attraction which exists between them. The weight of a body is shown by the pressure which it exerts upon its support; and Weight may be defined as the magnitude of the pressure which a body exerts upon its support. Weight is not the same at all points of the earth's surface, decreasing with the distance from the earth's center; for this reason a substance weighs less at the poles, because here the surface is flattened. *Weight* and *Mass* are not identical terms. The former is a measure of a *force,* the attractive force between the earth and some other body; while the latter is a measure of the quantity of *matter.* Again weight is a term that relates to our earth only, and is of variable magnitude even in that relationship; on the other hand, mass is entirely independent of place and is of invariable magnitude. It is therefore incorrect to speak of the *weight* of the earth, the *weight* of the sun, etc., but of their *mass.*

Mass and weight at places equally distant from the earth's center are proportional. Equal *masses* of Iron will *weigh* the same at the same place. The mass of a body and its weight have the following relation at sea-level:

$$M = \frac{W}{9.78}$$

The number 9.78 typifies the earth's acceleration and is

represented by the letter g, as follows:

$$M = \frac{W}{g}$$

Weight is, then, 9.78 times as large as mass. As all methods of measuring are only relative, and as mass and weight are proportional, we may measure both in the same terms—grams, kilograms, etc.

Measures of weight (terrestrial system). The unit of weight is the *gram,* which is the weight of a cubic centimeter of water (in vacuo) at 4 deg. C. The smaller denominations are one-tenth, one-hundredth and one-thousandth of this, and have the latin prefixes deci-, centi- and milli- respectively. The larger are multiples of the gram by 10, 100 and 1000 and have the greek prefixes deka-, hekto- and kilo- respectively.

One-thousandth gram—One Milligram.
One-tenth gram—One Decigram.
One-hundredth gram—One Centigram.
UNIT—ONE GRAM.
Ten grams—One Dekagram.
One hundred grams—One Hektogram.
One thousand grams—One Kilogram.

Measure of mass (absolute system). The unit of mass is the *gram,* which is the *mass* contained in one cubic centimeter of water at 4 deg. C. Its divisions bear the same names as the corresponding ones of the unit of weight, but in this instance they signify a *quantity* of matter. In ordinary reckonings the terrestrial system is used; while in scientific calculations the absolute is employed. One gram of mass equals 1:978 gram of weight.

VI. INDESTRUCTIBILITY is that general property of matter by reason of which, regardless of the changes a body or system of bodies may undergo, mass remains permanent. (*See law of the indestructibility of matter*).

VII. DIVISIBILITY. Every substance is divisible. But is there a limit to this, or can it be continued to infinity?

The answer to this question is of great importance to natural philosophy. From the times of the ancient greek philosophers two opposing theories regarding this have been held:

THE THEORY OF THE UNLIMITED DIVISIBILITY OF MATTER, which was held by those thinkers who claimed spirit and reason to be the only truths of existence, contends that, as we are able to divide to infinity, in thought, any substance of which we can conceive, it is also possible to divide material bodies in a like manner. The other

THE THEORY OF THE LIMITED DIVISIBILITY OF MATTER, which proposes that a body has certain component particles beyond which it cannot be divided, was advanced by those philosophers who claimed matter as the only entity.

At the beginning of the nineteenth century Dalton brought forward such strong proof in favor of the theory of the *limited* divisibility that scientists everywhere have accepted it; and under the name of *Dalton's Atomic Theory* it has become the foundation of modern chemistry. He noticed the constant combining-weights and formulated the laws of the constant, multiple and reciprocal proportions; and only when the theory of the limited divisibility of matter is assumed to be true can these three very remarkable laws be explained.

Let us call the smallest particles of matter atoms; these atoms, being real bodies, must have mass and weight. If we now assume that all atoms of the same element have the same weight, we furnish explanation of these three laws. Suppose that the weight of each atom of Hydrogen is 1, that of each atom of Oxygen 8 and that of each atom of Nitrogen 14, then a compound of Hydrogen and Oxygen containing one atom of each of these elements will always contain them in the weight-proportion of 1:8 (*law of the definite proportions*); and if a second compound of the two elements exists containing *two* atoms of the latter to one of the former, the weight-proportions will be 1:2x8; and if Nitrogen combines with Oxygen, the compounds formed will contain either one atom of Nitrogen (14 weight-parts) and one atom Oxygen (8 weigh-parts), or one atom of

Nitrogen (14 weight-parts) and *two, three, four or five* atoms of Oxygen, corresponding to 2x8, 16; 3x8, 24; 4x8, 32; or 5x8, 40 weight-parts of Oxygen (*laws of the definite, reciprocal and multiple proportions*).

With the establishment of the atomic theory it became necessary to distinguish between molecules and atoms.

A molecule is the smallest particle of matter which can exist in the free state and still remain chemically identical with the substance from which it is derived.

Molecules of water are still chemically water, molecules of salt are still chemically salt, molecules of sugar are still sugar; but they are the smallest amounts of water, salt and sugar which can exist. Molecules are extremely small—so small that it is impossible for the mind to conceive of their size; it is also impossible for us to really divide matter up into molecules by means of mortars, mills or the like. The smallest grain obtainable is a *mole*—a particle of measurable size—and is an aggregation of a great number of molecules. Molecular division can but be performed mentally and never physically. Let us mentally divide a chemical compound, say Potassium-iodide, into its molecules. These, although immeasurably minute, are still Potassium-iodide; and as this is a compound containing two elements, Potassium and Iodine, it can be still further split up into these components. The bodies resulting from such division are called atoms, which are thus seen to consist of single elements only.

An atom is the smallest particle of an element entering into a molecule.

Having seen that every real body has a mass, it follows that the atom and molecule also do so. These are the *molecular mass* and *atomic mass*. We assume the fact that all atoms of the same element have a like mass and therefore that all molecules of the same substance have the same mass also. It is evidently impossible to determine the real mass of the atom or molecule, and they are therefore stated as relative quantities, using the mass of an atom of Hydrogen as the standard of comparison for both molecular and atomic mass. When we say that the atomic mass of Oxygen is 16, it consequently means

that the atom of Oxygen has a mass 16 times as great as that of an atom of Hydrogen. The molecular mass of water is 18; that is to say, its molecule has a mass 18 times as heavy as an atom of Hydrogen.

The atomic mass of an element is the relative mass of its atom to that of the mass of an atom of Hydrogen.

The molecular mass of a compound is the relative mass of its molecule to the mass of an atom of Hydrogen.

The law of the indestructibility of matter requires that *the sum of the atomic masses be equal to the molecular mass of a compound.*

Hydrogen is taken as unit because it has the smallest atomic mass of all known elements. How the masses are determined will be given later; but the atomic theory requires that *the atomic masses of the elements are equal to their combining-weights, or are a simple multiple thereof.*

The atomic masses are given in the table of elements on page 6.

All bodies are made up of molecules, and it is assumed that there are forces which hold the atoms together in the molecule and the molecules together in the body. These are

Cohesion—the attractive force between like molecules; and

Adhesion—the attraction between the molecules of the surfaces of like or unlike bodies. Lead-plates *adhere* to each other when their smooth surfaces are pressed together; water *adheres* to glass and makes it wet.

Chemical Affinity is the attraction between atoms by virtue of which molecules are formed.

VIII. POROSITY is that property a body possesses by reason of small pores or interspaces contained within its mass. There are two kinds of such pores:

Sensible pores which can be seen, like those in sponge, pumice-stone, chalk, etc.; and

Physical or *Intramolecular pores* which cannot be seen but the existence of which is concluded from the fact that all bodies contract by cold and expand by heat.

IX. COMPRESSIBILITY is that property by virtue of which bodies are diminished in volume by pressure without loss of mass. It is a consequence of porosity. The most compressible bodies are gases.

X. ELASTICITY is the property by which matter resumes its original shape after having been compressed, twisted, bent or pulled.

XI. DENSITY. Different bodies may contain very varying quantities of matter in the same volume. One liter of Mercury weighs 13570 grams while a liter of water weighs but 1000 grams; Mercury is then said to be 13.57 times as *dense* as water. Hence, density is the relation of the mass of a substance to the mass of an equal volume of some standard substance. It is usually called *specific gravity*.

CHAPTER II.

SPECIFIC GRAVITY.

SPECIFIC GRAVITY of a substance is the relation of its weight to the weight of an equal volume of water. To determine it, *divide the weight of the substance by the weight of an equal volume of water.*

EXAMPLES:

What is the specific gravity of glycerine if a bottle holding 25 grams of it will only hold 20 grams of water?

$$25 \div 20 = 1.25.$$

Find the specific gravity of Mercury when equal volumes contain 50 grams of water and 680 grams of Mercury.

$$680 \div 50 = 13.6.$$

SPECIFIC VOLUME is the relative volume of equal weights of bodies, water at 4 deg. C. being taken as the standard of comparison. It can be calculated from the specific gravity and the specific gravity from it by *dividing the figure* 1 *by the specific gravity or the specific volume respectively.*

The specific gravity of alcohol is .82 ;find its specific volume.

$$1 \div .82 = 1.22.$$

What is the specific gravity of glycerine if its specific volume is 0.8?

$$1 \div .8 = 1.25.$$

From the preceding definitions it is evident that in order to determine the specific gravity of a body it is necessary to perform three operations: (a) to weigh it; (b) to weigh an amount of water equal in volume to the body under consideration; (c) to divide the weight of the body by the weight of the water. Evidently the second step is the most difficult one; for if

the substance in question be a solid of irregular shape, it is impossible by ordinary means to ascertain its true volume—which must be done in order to weigh an equal volume of water. In such cases calculations are based upon the "*Archimedes' Principle.*" It reads: *If a body be immersed in a liquid, it loses a weight equal to the weight of the liquid displaced.* If we weigh the body when immersed and note its loss of weight, we know that

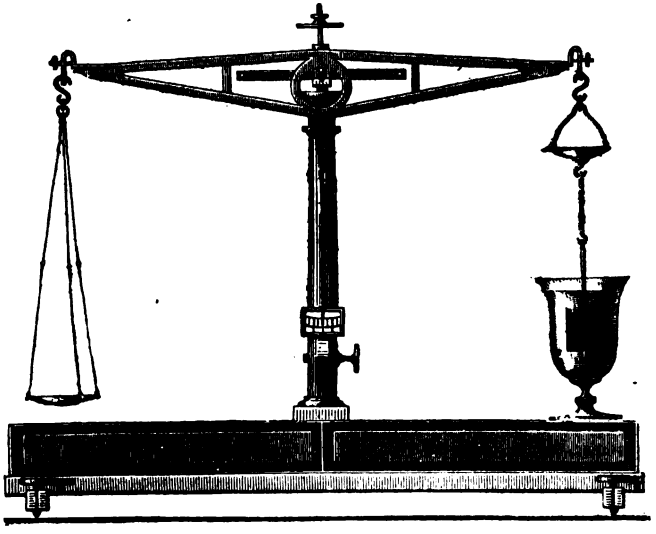


FIGURE I.

it has a volume equal to that of a body of liquid whose weight is the same as this weight-loss.

DETERMINATION OF THE SPECIFIC GRAVITY OF SOLIDS.

1. Of those heavier than water and insoluble in it.

(a). *By means of the hydrostatic balance.* A hydrostatic balance is constructed like an ordinary chemical balance, except that the suspension of the pan on the right side is not as long as the one on the left and has on its bottom a hook (fig.1). The

substance is suspended on this by means of a wire and its weight ascertained. It is then immersed in water, and will now weigh less. The weight-loss undergone is, according to the Archimedes' principle, equal to the weight of an equal volume of water. Therefore the weight in air, divided by the weight-loss in water, gives the specific gravity.

EXAMPLE:

A body weighs, in air, 15 grams; submerged in water, 10 grams. What is its specific gravity?

It weighs, in water, 5 grams less than in air; hence

$$15 \div 5 = 3.$$

(b). *By means of Nicholson's areometer, or waterbalance*; this is a hollow instrument made of glass or tin in the shape shown in figure 2, and placed in a vessel filled with water. The lower end is weighted to maintain the instrument in an upright position and carries a small basket. From the upper end a vertical rod extends, bearing a graduation mark (o) and having on top a disc which corresponds to the scale-pan of a balance. The instrument is immersed up to the graduation mark In order to keep it at this point, weights have to be put on the disc and these are called the capacity of the balance. Then the body whose specific gravity is to be determined is placed on the disc and the apparatus will now sink in the water. Weights sufficient to allow it to rise again to the mark are removed, and these are equal to the weight of the substance in air. The body is then placed in the basket and, immersed in the water, is buoyed up to a certain extent. Additional weights are placed on the disc sufficient to sink the instrument to the graduation line again and, according to Archimedes' principle, these are equal to the weight of the water displaced. Now divide the weight of the substance in air by the weight-loss in water and obtain the specific gravity.

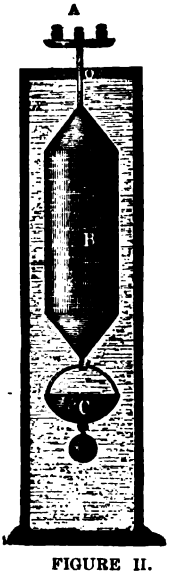


FIGURE II.

Suppose that the capacity of the instrument is 50 grams

and that after placing the substance on the disc and removing weights sufficient to bring the rod to the graduation-mark only 40 grams of the capacity is left, showing a weight in air of

$$50 - 40 = 10 \text{ grams.}$$

and that when the substance is placed in the water it needs 42.5 grams on the disc to restore equilibrium, showing a weight-loss in water of

$$42.5 - 40 = 2.5 \text{ grams.}$$

then the specific gravity is

$$10 \div 2.5 = 4.$$

(c). *By means of a pyknometer* (fig.3). This is a glass bottle having a graduation on its neck for a specified amount of water and having a perforated glass stopper which, when inserted into the neck, reaches exactly to the graduation-mark. The instrument is filled with water and the stopper introduced; the excess of water passing out through the perforation. The total weight is then determined by a chemical balance; then the solid is weighed in air. The solid is now placed in the bottle of water, some of which will flow out; and this, of course, has an equal volume to that of the solid immersed. The bottle is stoppered and is found to weigh less than the sum of the weights of the solid and of the water; the loss in weight corresponding to the weight of a body of water equal in volume to the solid. Dividing the weight of the substance in air by the weight of an equal volume of water gives the specific gravity.

EXAMPLE: The bottle filled with water weighs 50 grams, the solid substance in air, 5 grams. When the solid is introduced into the bottle, the weight is 52.5 grams; find the specific gravity of the substance.

The solid substance and the bottle filled with water weigh 5 grams and 50 grams respectively, or 55 grams in all. When the substance is placed in water, some overflows; it now weighs only 52.5 grams; hence 2.5 grams of water ran out. The specific gravity is therefore

$$5 \div 2.5 = 2.$$

2. Of Solids lighter than water.

(a). *By the sinker method.* Weigh a piece of Platinum or glass (the sinker) in air and then immerse in water and observe the loss of weight there. Dry the sinker and weigh in air together with the solid; the difference between the combined weight and that of the sinker alone gives the weight of the solid in air. Weigh both in water—the heavy sinker will draw the lighter solid below the surface, this giving the total weight-loss of the two together in water; and when the weight-loss of the sinker alone is subtracted from this, the weight-loss of the solid in water is found. Divide the weight-loss of the solid in air by the weight-loss it suffers in water to obtain its specific graviy.

EXAMPLE:

Sinker in air	50 grams
Sinker in water	45 grams
Sinker lost in water	5 grams
Sinker and substance in air	54 grams
Sinker alone in air	50 grams
Solid in air	4 grams
Sinker and solid in air	54 grams
Sinker and solid in water	43 grams
Sinker and solid lost in water	11 grams
Sinker alone lost in water	5 grams
Weight-loss of solid alone in water	6 grams

Weight of solid in air (4 grams) divided by its weight-loss in water (6 grams), shows a specific gravity of 0.6667.

(b). *Method of immersing a body in a liquid which is lighter.* Any of the methods given under 1 may be used, substituting for water a liquid in which the body will sink and in which it is insoluble. If the calculations are made in the manner there shown, an erroneous specific gravity will be obtained because

the standard of comparison is water, which has a different power of buoying up, volume for volume, than has the liquid used in this instance. To correct this, multiply the figures obtained by the specific gravity of the liquid used.

EXAMPLE:

Solid in air	5 grams
Solid in Benzine	1 gram
Loss in Benzine	4 grams

FIG. III.

Specific gravity in relation to benzine is

$$5 \div 4 = 1.25.$$

But the specific gravity must be stated in relation to water; and as the specific gravity of benzine is 0.67 (relative to water), the correct figures are obtained on multiplying by this:

$$1.25 \times 0.67 = 0.8375.$$

3. Of solids soluble in water.

Use any of the above methods, substituting for water some liquid in which the solid is insoluble and will sink and correct the erroneous specific gravity as just explained.

DETERMINATION OF THE SPECIFIC GRAVITY OF LIQUIDS.

(a). *By means of a pyknometer* (fig.3). Weigh the bottle when empty and again when filled with the liquid; subtract the weight of the empty bottle and find the weight of the liquid contained. Fill the same bottle with water and weigh; subtract the weight of the empty bottle and obtain the weight of the water the bottle holds. The weight of the liquid, divided by that of the same volume of water gives the specific gravity.

EXAMPLE:

Bottle filled with liquid	35 grams
Bottle empty	20 grams
Weight of liquid alone	15 grams

Bottle filled with water	30 grams
Bottle empty	20 grams
Weight of water alone	10 grams

Then 15 ÷ 10 = 1.5. Specific gravity.

A very convenient pyknometer for determining the specific gravity of liquids is that of *Sprengel* (fig. 4). It is first weighed while empty. It is then filled by suction with the liquid and suspended in water of standard temperature until the volume of the liquid becomes stationary. A piece of filter paper is then held to the end of one of the narrow shanks and enough liquid drawn out to bring it just to the graduation mark in the other shank. The apparatus is then suspended on the hook of a chemical balance and weighed. Subtracting the weight of the empty instrument we obtain that of the liquid the bottle holds. The process is repeated, this time using water in the instrument. Comparison of the two weights will now give the specific gravity of the liquid.

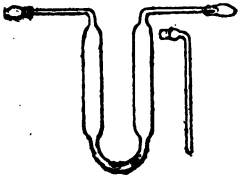


FIG. IV.

(c). *By means of a Mohr's or Westphals' balance.* (*fig.* 5). This is a hydrostatic balance in which a thermometer acts as sinker. It is evenly balanced in air, but when the sinker is immersed the scale is tipped by reason of the buoyancy of the water. The beam is divided into ten equal parts and has weights in the shape of hooks, which can be suspended at any of the various division-marks. The heaviest of these is so constructed that when suspended at the tenth mark it restores equilibrium if the sinker is immersed in water. The other weights are equal to one-tenth, one-hundredth and one-thousandth of this. The heaviest weight, therefore, when suspended at the tenth division mark, represents a weight of water having the same volume as the immersed sinker.

Immerse the thermometer in the liquid and adjust the weights until equilibrium is restored. The specific gravity, as recorded by the hook-weights, can be then directly read off.

(d). *By means of hydrometers* (fig. 6). These consist of hollow glass tubes having a bulb at one end filled with shot or Mercury so that the instrument will remain upright when immersed. They are graduated by immersing in different liquids of known specific gravity and marking this on the tube each time. As the instrument sinks deeper in light than in heavy liquids, the figures on the scale become smaller upward and larger downward. For convenience two classes of hydrometers are used.

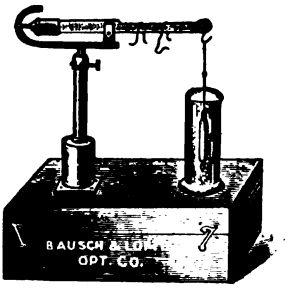


FIG. V.

For liquids of high specific gravity—these are graduated with the specific gravity of water (1) at the top, the higher specific gravities running down from this.

For liquids of low specific gravity. Bearing the graduation for water (1) at the bottom and being graduated above this with the lower specific gravities.

Special kinds of hydrometers. Urinometers (used to determine the specific gravity of urine) have markings from 1.000 to 1.060. Lactometers or lacto-densimeters are instruments used to determine the specific gravity of milk; alcoholometers are hydrometers employed to determine the percentage of alcohol and are graduated by immersing in pure water, 1 percent alcohol, 2 percent alcohol, etc., and marking accordingly. There are two alcoholometer scales, one recording weight percentage, for which Richter's alcoholometers are used, and the other recording volume percentage, which is determined by Tralle's alcoholometer.

INFLUENCE OF HEAT UPON SPECIFIC GRAVITY.

The specific gravity of a substance becomes smaller when warmed, on account of the expansion it suffers; a fixed temperature is therefore necessary. This is usually 15 deg. C. or 59 deg. F. The United States Pharmacopoeia of 1900 gives 25 deg. C. as the standard except for alcohol and wine, which are measured

at 60 deg. F. on account of the custom-house regulations. Below are a few specific gravities which it is desirable for the student to learn:

Water (4° C.)	1.000	Aluminum	2.583
Alcohol (25° C.)	.809	Iron	7.740
Ether	.716	Gold	19.320
Chloroform	1.476	Silver	10.500
Mercury	13.570	Hydrochloric acid	1.158
Platinum	21.400	Sulphuric acid	1.826
Bromine	2.990	Nitric acid	1.403

DETERMINATION OF THE SPECIFIC GRAVITY OF GASES.

Hydrogen or air is used as standard, this being more convenient. As air is 14.43 times as heavy as Hydrogen, the specific gravity of a gas in relation to Hydrogen is 14.43 greater than in relation to air.

FIG. VI.

The volume of gases is much more influenced by changes of pressure than is that of liquids or solids, and in the determination of the specific gravity of a gaseous substance great care must be taken to ensure exactitude. If not measured under like conditions of temperature and pressure, due allowances must be made. We cannot give here the technique, but refer the student to more exhaustive textbooks on physical chemistry for their thorough study.

CHAPTER III.

THE THREE STATES OF MATTER

All matter exists in one of three conditions; it is solid, liquid or gaseous.

SOLID BODIES are substances which retain their shape. The cohesion existing in them is so great that force is necessary to change their form and as force is also necessary to produce a change in their volume (e. g., when they are compressed), we may state that

Solid bodies are substances which have an independent form and offer resistance to both change of their form and of their volume.

LIQUIDS are those substances which have no shape of their own, but which assume that of the vessel containing them—excepting on the surface, which is a level. Cohesion exists in liquids also, but is not sufficient to resist the earth's attraction, which compels the molecules to fill all inequalities of the bottom of the container. When liquids are not under the influence of the earth's attraction, they assume a globular shape, proving that molecular attraction or cohesion acts in them . A liquid at the earth's surface cannot offer resistance to change of its form, as can a solid; but only to change of its volume. Therefore we may state that

A liquid is a substance which offers resistance to changes of its volume but not to changes of its form.

Not always is the surface of a liquid under the influence of the

earth's attraction a level. When the liquid is contained in a narrow tube, it is seen to be curved.

A Meniscus is the curved surface of a liquid in a narrow tube. Its appearance in the compression-tube is taken as significant of the liquifaction of a gas and its disappearance indicates the conversion of a liquid into a gas. The meniscus may be concave or convex. It is concave when the liquid is able to moisten the tube, as is the case with water in glass tubes; and convex when the liquid cannot moisten the tube, as in the case of Mercury in glass tubes.

The surface of liquids not being level, it becomes necessary to decide which point of the meniscus is to be used in computing in graduated tubes, burettes, pipettes, barometers, etc. In chemical work, the following rules are generally adopted:

1. If the meniscus is convex the highest point of the meniscus is taken as the reading point.

2. If the meniscus is concave, two different conditions govern the reading:

(a). If the liquid is colorless, or nearly so, and perfectly transparent, the lowest point of the lowest zone is used, this being the most easily observable.

(b). If the liquid is colored and not perfectly transparent, it is difficult to see the lowest point and the line where the liquid touches the container is used.

Very narrow tubes are called *capillary tubes* (hair tubes).

When a capillary tube, open at both ends, is placed with one of its ends in a liquid, the liquid is seen to stand at a different level on the inside of the tube than on the outside. Water in glass tubes stands higher inside than outside, while Mercury in glass tubes stands lower inside. This phenomena by reason of which liquids are elevated or depressed in open capillary tubes is an instance of *capillarity* or *capillary attraction*.

Upon investigation we find that only when the liquid is able to moisten the tube does it stand higher inside than out; and that when it is incapable of wetting the tube, it is *lower* on the inside. Hence capillary elevation coincides with a concave, capillary depression with a convex meniscus.

Many phenomena observed in our daily life are due to capillarity. The fact that sap rises in plants, water in a sponge, oil or melted wax in the wicks of lamps and candles, water in a piece of sugar, etc., are every-day examples.

GASES are substances which may be said to have no or very little cohesion; for their molecules tend to disperse and separate from each other as far as possible. Thus, however small the mass of a gas enclosed, it will fill the container entirely, although the molecules may be widely separated from each other. It appears as if a repulsive force in each molecule tends to drive one away from the other. This property of dispersion or expansion to the limits of the space containing them is characteristic of all gases. They have no form of their own but assume that of the container. All gases are not like air, odorless, colorless and tasteless. Chlorine is yellowish-green in color; Iodine vapors are violet; Nitrogen dioxide and Bromine vapors are brown and Chlorine, Nitrogen dioxide, Ammonia, Hydrogen-chloride, Hydrogen-sulphide and other gases have all characteristic odors and tastes.

The *tension* of a gas is the pressure it exerts upon the walls of its container. It is caused by the tendency of gases to expand infinitely.

Diffusion of gases is that property whereby all gases tend to mix with each other in every proportion, until there is a uniform mixture. Even when two gases are placed in different bottles and these connected by a narrow tube of considerable length, the transmigration of the two gases will take place; any two gases are miscible. Diffusion results from the tendency of gases to expand, the molecules of each endeavoring to get as far off from other molecules as possible and thus entering the spaces between each other until all are equally mixed.

Law of the diffusion of gases. Gases of high specific gravity diffuse slower than those of low specific gravity, according to the following law:

The time which equal volumes of any two gases require to diffuse is proportional to the square roots of their specific gravities.

Effusion is the passage of a gas through minute openings in a thin wall. It complies with the same laws as diffusion.

Bunsen used the law of effusion for the determination of the specific gravity of gases. The method is briefly as follows: First a certain amount of a gas is permitted to effuse through a fine opening and the time required is ascertained; then the same volume of air (the specific gravity of which is known) is also permitted to effuse through the same opening and the time consumed is again noted. The rate of effusion and the specific gravity of one of the gases being known, that of the other can be easily computed.

Atmolysis is the process of separating mixed gases having different specific gravities and is based upon the difference in their rates of diffusion through porous material. Hydrogen is 16 times as light as Oxygen. If we slowly pass a mixture of these two gases through long tubes of porous material—say clay pipestems—the Hydrogen, having the lower specific gravity, rapidly diffuses through the pores; while the Oxygen, on account of its high specific gravity, does not diffuse. On collecting the gas after it has passed through the tubes it will be found to be almost pure Oxygen. Air is a mixture of Nitrogen and Oxygen and the fact of the latter having a higher specific gravity than the former has led to attempts at preparing Oxygen from air by means of atmolysis.

Weight of gases. Gases have weight, like all other bodies, but as it is very small when compared with that of equal volumes of liquids or solids, its determination requires many precautions. It is, nevertheless, one of the most important chemical operations.

Atmospheric pressure. The weight of a gas causes it to exert pressure upon its support. We speak, for example, of an atmospheric pressure or air pressure of a certain number of grams meaning by this the pressure which an air-column, having a transverse section of one square centimeter and reaching from the earth to the upper limits of our atmosphere, exerts upon one square centimeter of the earth's surface.

The Barometer is an instrument for measuring this pressure. It consists of a U-shaped glass tube one of the branches of which is much longer than the other. The longer branch, which

is closed at the top, is filled with Mercury; while the shorter one is open and serves as a reservoir for the Mercury which may flow out of the other. When stood upright, with the closed end upward, the Mercury will fall in the longer arm until it stands about 760 millimeters above the surface of the Mercury in the shorter arm. A column of air reaching to the upper most limits of the atmosphere, now rests upon the surface of the Mercury in the open arm and tends to drive this back into the closed arm. But to do this, it must lift up the column of Mercury herein contained, which exerts a force tending to equalise the height of the surface in both arms of the tube. As no more Mercury flows out when the surface in the longer arm has reached a point 760 millimeters above that in the open shank, we must conclude that the weight of the Mercury column in the one arm and that of the air-column in the other counterbalance each other; or that a column of air, reaching from the surface of the earth to the limits of our atmosphere, has the same weight as a column of Mercury 760 millimeters long and having a transverse section equal to that of the column of air. The weight of such a column of Mercury, if the transverse section be one square centimeter, is 1.033 kilograms; therefore the atmospheric pressure is 1.033 kilograms on each square centimeter of the earth's surface.

This is not constant either at all points of the earth's surface or at the same place at different times. The greater the distance above the sea-level, the lower the Mercury in the barometer. At the sea-level this is usually, as we have seen, 1.033 kilograms per square centimeter; or equal to the height of a Mercury-column of 760 millimeters (30 inches).

APPARATUS FOR THE MANIPULATION OF GASES.

There are three kinds of such apparatus:

1. *Apparatus for generating gases.*
2. *Apparatus for purifying gases.*
3. *Apparatus for collecting gases.*

APPARATUS FOR GENERATING GASES.

Apparatus for generating gases are again divided into:

(a). *That for dry generation*—when the gas is generated

from dry substances by heat, as in the production of Oxygen from Potassium-chlorate. Retorts made of iron, copper, glass, etc., are used in which to heat the dry substance.

(b). *Apparatus used for liquid generation*—when the gas is obtained from liquids, or from the contact of a liquid and a solid, as in the production of Carbon-dioxide from the contact of marble dust and Hydrochloric acid. Here a flask is used, into which the solid is introduced. The mouth is tightly closed by a doubly-perforated stopper, through one hole of which a right-angled tube passes to conduct the generated gas to the purifying apparatus; and through the other hole a long funnel-tube which reaches nearly to the bottom of the flask. The liquid is

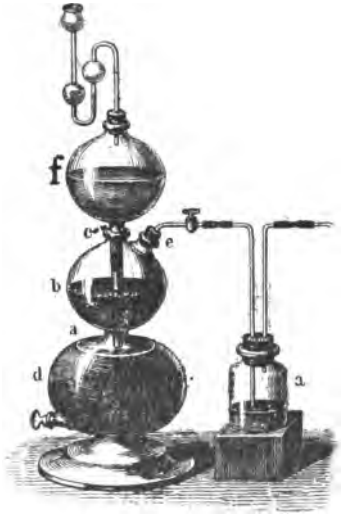


FIGURE VII

poured in through this tube until the lower opening is closed. The flask is then heated, if heat be necessary.

The apparatus in most general use in chemical laboratories for the cold generation of gases by the contact of a solid and a liquid is the *Kipp's apparatus.*

It consists of two separate parts (fig. 7). The foot is made up

of two glass globes, b and d, which are connected by a narrow neck. The lower globe has an opening, closed by a glass-stopper, by means of which the liquid can be emptied out. The upper globe, b, has a side-opening, e, closed by a rubber stopper through which a glass tube, having a stopcock, passes. The mouth of the globe b is ground to receive the upper part of the apparatus. This consists of a glassglobe, elongated at the bottom so as to form a narrow tube which reaches down so as to fit into the neck of globe b, and reaches the bottom of globe d as shown in fig. 7. The mouth of this is closed by a cork having a bent safety-tube inserted into it.

The working principles are as follows: the solid substance is filled into b through the tube e, the pieces being large enough not to pass through the neck between b and d. The liquid is filled in through the mouth of f. When the stop-cock is opened the liquid runs through the tube c into the globe d, fills it, flows up through the neck into b, which contains the solid, and gas is generated. When the cock is closed the gas presses upon the liquid and drives it back into f, thus interrupting the generation.

APPARATUS FOR PURIFYING GASES.

Apparatus for purifying gases are of two kinds:

(a). *Washing apparatus.* In order to purify a gas it is passed through a wash-bottle. This is a wide-mouthed bottle containing water or other suitable liquid and is tightly closed by a cork having three perforations. The middle hole is fitted with a long, straight tube open at both ends—the lower reaching nearly to the bottom of the bottle. The object of this will be explained later (see safety tubes). In one of the other holes is fitted a right-angled tube reaching nearly to the bottom of the bottle and being connected to the generator by rubber tubing; this serves to conduct the impure gas into the wash-bottle. The third hole carries another right-angled tube which passes just through the cork, the other end being connected with the apparatus in which the gas is to be collected. The gas generated passes in bubbles through the water in the washbottle, there losing its impurities.

A so-called *Woulff's bottle* may be conveniently used for this

purpose. This has three separate necks to accomodate the three different tubes entering it.

(b). *Drying apparatus.* A gas, after passing through the washbottle, contains more or less water in the form of vapor. Drying is accomplished by means of certain substances which absorb and retain moisture. Examples of these substances are concentrated Sulphuric acid, which is a liquid, and Calcium-chloride, which is a solid. When Sulphuric acid is used as a drying medium, any kind of wash-bottle can be used, the acid being poured into the bottle and the gas passed through it.

To effect the drying of gases by means of Calcium-chloride, tubes (called *Calcium-chloride tubes*) are used; these are either straight or U-shaped. Small pieces of Calcium-chloride are introduced and one end of the tube is connected with the collecting apparatus, the other with the generator. As the gas passes through, it is robbed of its moisture.

APPARATUS FOR COLLECTING GASES.

These comprise

(a). *Those in which gases are collected in gaseous condition.*

The simplest apparatus of this kind is the *pneumatic trough.* It consists of a dish made of tin, porcelain, glass or other suitable material filled with a liquid. Below the surface of this a vertical bridge is fastened, having a hole through its center. A bottle is then completely filled with the same liquid, tightly closed by a cork and inverted over the hole in the bridge—its mouth being under the surface of the liquid. The liquid is prevented from escaping by the atmospheric pressure. The tube leading the gas from the generator is immersed in the pneumatic trough and placed through the hole in the bridge. The gas ascends in bubbles up into the bottle, where it displaces the liquid and eventually fills the bottle. It is then corked while still below the surface and removed. Fig. 8 illustrates the generation, washing and collecting of a gas.

In addition to the above, gas-bags and gasometers are employed for the collection of gases.

(b). *Apparatus by which gases are collected in solution.* Many gases are soluble in liquids, some in high degree, others

but slightly . The fact that it is more difficult to handle gases than liquids makes it preferable for practical purposes to use solutions of gases where possible, especially when soluble in water. The more common of these handled by the chemist are Ammonia-water, Chlorine-water, Hydrochloric and Sulphurous

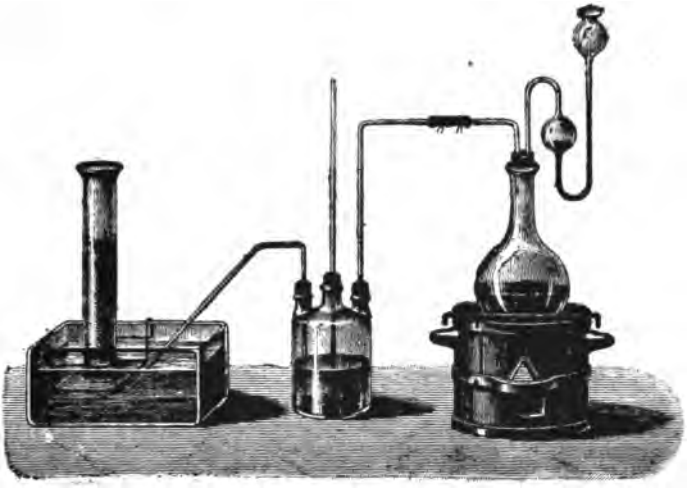


FIGURE VIII

acids. These solutions are made in laboratories in the following manner:

The outlet tube of the wash-bottle is connected by rubber tubing with a right-angled tube which goes down to the bottom of a bottle containing cold distilled water. This is called the *absorption* or *receiving bottle.* The gas has to pass through the water and much is absorbed. To complete absorption, the bottle is repeatedly shaken. Fig. 9 illustrates an apparatus used for generating, washing and dissolving gases.

Safety tubes.

Some gases (Ammonia, etc.) are so freely soluble in water that all in the wash-bottle and tubes is almost instantly dis-

solved, creating a vacuum in the apparatus. As a result, the air pressure on the water in the absorption-bottle forces it back through the tube into the wash-bottle, and from here into the generating flask. Such an accident would surely spoil the preparation and might destroy the apparatus; so to avoid this the third tube is placed in the wash-bottle. When the pressure becomes less than that of the external air, the latter drives the liquid in this tube into the bottle, and when the tube becomes

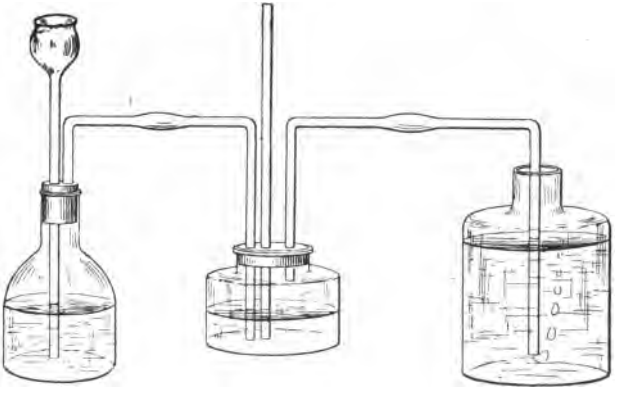


FIG. IX

empty, air passes through it into the wash-bottle until the pressure is equalised. This is called a *safety-tube.*

The funnel-tube in the generating flask also serves as a safety-tube, preventing the liquid from being driven back into the generator by equalising the internal and external pressure in the same manner.

These tubes also prevent the apparatus from explosions caused by *increase* of pressure within the apparatus. One of the tubes may become accidently closed; this, with the continued generation of gas, will *raise* the liquid in the tube and it will flow out until the surface of it in the apparatus is so much lowered that a communication is established with the outside air and pressure is equalised.

Difference between gases and vapors. The examination of gaseous substances regarding the effect of pressure upon them reveals a difference between them which divides them into two distinct classes:

1. Those which, when compressed while the temperature is kept stationary, at first decrease in volume, then become liquid if the pressure be further increased; they are called *vapors.* An example is Carbon-dioxide. This gaseous substance can be made liquid at any stationary temperature below 31° C. by merely increasing the pressure upon it. Another example is water-steam at 110° C., which, if sufficient pressure be applied and the temperature kept at 110° C., will liquify.

2. Those gaseous substances which it is impossible to convert into liquids by pressure alone if the temperature is not reduced. If the ordinary temperature of air be maintained throughout the experiment, the utmost pressure it is possible to apply will not liquify it. Gaseous substances which exhibit this characteristic are termed *true gases.* Air, Oxygen, Hydrogen and Nitrogen are true gases.

Some years ago it was found that if their temperatures are lowered sufficiently, they too can be liquified by pressure. Below —140° C. air can be brought to the liquid state by sufficient pressure; so that air, below —140° C., is a vapor, for it can be liquified by pressure alone. True gases thus become vapors when the temperature falls below a certain degree, which is called their *critical temperature;* then

Critical temperature or *absolute boiling point* is the temperature below which it is necessary to cool a true gas in order to liquify it by compression. It may be also defined as the temperature above which no pressure can prevent a volatile liquid from passing into the gaseous state.

The effect of heat upon vapors is to cause them to become true gases when their critical temperature is reached; because then the pressure alone, without simultaneous reduction of temperature, does not liquify them. Each gaseous substance and volatile liquid has its individual critical temperature. The critical temperature of air is —140° C., that of Carbon-dioxide is 31° C., etc.

The *critical pressure* is that required to liquify a gas when infinitessimally below its critical temperature. At the critical temperature a gas cannot be liquified by this pressure, but passes into a condition midway between the liquid and gaseous called the *critical condition.* In this state the substance has already decreased in volume to that of the liquid form, but no meniscus is observable (this is characteristic of the liquid condition). The smallest decrease of temperature will convert it into a true liquid, the smallest increase changes it into a true vapor.

Vapors are either

Saturated—When a space has acquired all the vapor which it can contain it is said to be saturated. The smallest increase of presure causes a liquifaction of a portion of the saturated vapor. The higher the temperature, the greater the quantity of vapor which a certain space may acquire; or

FIG. X

Unsaturated—When a space can take up more vapor is not yet saturated An unsaturated vapor must first become saturated by compression before it will liquify.

Condensation is the process of liquifying gases. All gaseous substances are capable of liquifaction by pressure, by cold, or by the two combined. The method which is used depends upon the critical temperature and boiling point of the resultant liquid.

Condensation is the process of liquifying gases. All gaseous substances can be liquified by pressure, by cold, or by the two together. The method which is used depends on the critical temperature and boiling point of the resultant liquid.

(a). If this has a high boiling point, cooling will condense the gaseous substance. Water-steam condenses when cooled below 100° C. (see *distillation*).

This method can be used even if the liquid has a boiling point which is below ordinary temperature, but not below —20° C. The gas is passed through tubes placed in a freezing mixture (as crushed ice and salt), which causes it to condense.
The apparatus shrown in fig. 10 is well adapted for this purpose.

(b). If a gas has a critical temperature above the ordinary but a boiling point lower than can be reached by a freezing mixture, like Ammonia, Cyanogen, Chlorine, etc., it can nevertheless be liquified in the above fashion when pressure is applied at the same time. This is especially easy when they are generated by heating a dry solid, as in the manufacture of Di-cyanogen by heating dry Mercuric-cyanide, or Ammonia by heating Silver-ammonium-chloride. A little of the dry substance is placed in a thick-walled tube bent at a right-angle (fig.11). The open end of the tube is then sealed by fusion. If that end of the tube which contains the dry substance is now heated, and the other end placed in a freezing mixture, the gas formed will condense by the cold and by the pressure caused by the continued generation of the gas.

(c). If a gas has so low a critical temperature and the corresponding liquid has so low a boiling point that they cannot be reached by ordinary freezing mixtures, (this occurs in the case of Oxygen, Hydrogen, Nitrogen and other gases), the condensation is difficult and can be performed only by large machinery. Two principles are applied to this object:

When a highly compressed gas is permitted to expand suddenly, a great reduction of temperature takes place, allowing a portion of the gas to liquify.

This method of cooling is called *internal refrigeration.* M. Cailletet first used this method for the liquifaction of gases. An application of the same idea is made by Prof. Linde and others to a practical method for the making of large quantities of liquid air at comparatively small expense.

When a volatile liquid spontaneously evaporates, cold is produced. Especially when liquified gases like Ammonia, Sulphur-dioxide, Carbon-dioxide, etc., are used is the reduction

of temperature remarkable. Liquified Carbon-dioxide, vaporising in air under ordinary pressure, has a temperature of —78° C.; but when it vaporises in vacuo this diminishes to —140° C. The cold produced by the vaporisation of a liquid whose corresponding gas is readily condensed, may be used, together with pressure, for the condensation of gases which are more difficult to condense; and the liquids obtained may be used in turn to furnish by their vaporisation the cold necessary for the liquifaction of gases extremely difficult to condense.

This method has been applied by Pictet and others to the liquifaction of Oxygen. The gas is obtained by heating a dry solid and then compressed by its own pressure into strong iron tubes placed in tanks in which liquified Carbon-dioxide circulates, vaporising in a vacuum. The vaporisation of the liquified

FIG. XI

Carbon-dioxide reduces the temperature to below the critical point for Oxygen, and it condenses.

Preservation of liquified gases. Those which have a relatively high boiling point can be kept in sealed glass tubes. Others like liquified Carbon-dioxide, Ammonia, etc., are kept in steel drums of great strength. Some exert such enormous pressure that it is extremely difficult to retain them in any container at present devised. It is safest to keep these in open vessels; but as their boiling points are far below ordinary temperature, they boil permanently. To retard this, a container has been constructed by the English chemist Dewar and this is known as the *Dewar's bulb.* It consists of an open globe-shaped glass vessel having double walls. The space between these is a vacuum

and does not permit of the conduction of heat from the outside to the liquified gas. The innermost wall is coated on its external surface with a thin film of Mercury amalgam to prevent the admission of radiant heat, which this surface reflects before it can act upon the liquified gas. In this manner conduction and radiation of heat are reduced to a minimum and the liquified gas keeps fairly well in the interior.

BOYLE' LAW (*also called Mariotte's law*).

Pressure always decreases the volume of bodies whether they be solid, liquid or gaseous; but gases behave entirely different to solids or liquids. The same pressure applied to different solids or liquids produces widely diverse changes of volume, as rubber, wood and iron show. The same pressure on different gases, however, equally compresses all. If one liter of Hydrogen, one of Oxygen and one of Carbon-dioxide all be measured at one atmospheric pressure and then the pressure doubled, their volumes will still be equal. Indeed, when the pressure is doubled, they decrease to just half of their original volume; and if the pressure be made three times as great their volume is reduced to one-third. They are always affected in this ratio; that is

Pressure	Volume	Product.
1 atmosphere	1 liter	$1 \times 1 = 1.$
2 atmospheres	½ "	$2 \times ½ = 1.$
4 "	¼ "	$4 \times ¼ = 1.$

Multiplied together, the product is always the same.

That is

$$P \times V = p.v$$

$$\text{or } P \times V = \text{constant}$$

We therefore have the law:

All gases are equally compressed by the same pressure and the product of the volume they occupy and the pressure at which the volume is measured is constant provided the temperature is maintained unchanged.

CHARLES' LAW (*also called Gay-Lussac's first law*).

Increase of temperature expands all bodies, whether solids,

liquids or gases; but a close study of the expansion of gases by heat reveals the remarkable fact that they are all expanded alike by equal increments of heat, while the amount of expansion of liquids and solids by heat varies greatly and depends upon the chemical nature of the substance. If we further investigate the amount of expansion which a gas suffers when heated 1° C., we find the following law to operate:

All gases, when heated without pressure change, expand equally and for each C. degree they are heated above zero, they expand 1-273 (0.003665) *of their volume at that temperature.*

The quantity 1-273 is called the *expansion coefficient of gases.*

One liter of a gas, measured at 0° C., expands 0.003665 liter when heated 1° C.; if heated t° C., it expands (0.003665 x t) and therefore measures, (1 + 0.003665 t) liters. Then if Vo liters (measured at 0° C.) be heated t°, the volume V, at t°, equals the volume at 0° C., multiplied by 1 + 0.003665t:

$$V = Vo(1 + 0.003665t).$$

Physics proves that all heat motion ceases at —273° C., and many scientists use thermometers having this degree as zero. These record absolute temperatures and therefore 0° C. corresponds to 273° absolute, or t° C. equals T — 273. (t is used to signify the ordinary degrees and T the absolute). Placing this value of t in the formula of Charles' law, we obtain

$$V = Vo\left(1 + \frac{T - 273}{273}\right).$$

$$V = Vo\left(1 + \frac{T}{273} - 1\right)$$

$$V = \frac{Vo.T}{273}$$

This equation shows that Charles' law may also be expressed as follows:

The volume of any gas under constant pressure is proportional to the absolute temperature.

COMBINED BOYLE'S and CHARLES' LAWS

Let V equal the volume of a gas at t° C. and P the pressure; then Vn may equal the volume of the gas at normal pressure (760 mm.) and 0° C. If first the pressure be neglected, we have according to Charles' law,

$$V = Vn\ (1 + 0.003665\ t\ )$$

But according toBoyle's law, the equation remains correct if we multiply V and Vn by the pressures belonging to them

$$V.P = Vn(1 + 0.003665\ t)\ 760$$

$$V = \frac{Vn(1 + 0.003665t)\ 760}{P}$$

This equation is also of great importance, and allows the changes of volume suffered by gases caused by pressure and temperature to be calculated.

Change of the tension of a gas by heat. It is evident that the expansion of a gas by heat can be prevented if the gas is enclosed in a strong enough container. The heated gas will certainly press the harder on the vessel—the *tension* of the gas will be *increased.* The magnitude of this increase of tension for each degree C. can be easily calculated from the formula of the combined Boyle-Charles' laws:

$$V.P = Vn\ (1 + 0.003665t)\ 760$$

If the volume remains stationary, V =Vn and the formula becomes

$$P = (1 + 0.003665t)\ 760$$

This equation demonstrates that

All gases, when heated and their volume maintained unchanged, increase their tension equally; and for each degree C. the tension is increased 0.003665 *of that existing at zero.*
The law is substantiated by experiments.

AVOGADRO'S LAW.

Granting the correctness of the laws of Boyle and Charles, Amadeo Avogadro, observing the entirely dissimiliar effects

produced by heat and pressure upon different bodies, questioned *why* all gases thus regularly conform to changes of pressure and temperature. He advanced the following explanation:

The molecular arrangement of all gases is identical; equal volumes of all gases, when measured at like temperature and pressure, contain the same number of molecules.

For the true chemist a thorough understanding of this law in all its bearings is essential, as upon this law chemistry is largely based.

Relation of the molecular mass of a gas to the density.

Equal volumes of two different gases—say 1000 cc. of Hydrogen and 1000 cc. of Oxygen—both at 0° C. and 760 mm. pressure, according to Avogadro's law, contain the same number of molecules: the 1000 cc. of Hydrogen weigh 0.0895 grams and the 1000 cc. of Oxygen weigh 1.429 grams.

We will assume that the volume of Hydrogen contains n number of molecules; therefore each molecule of Hydrogen weighs 0.0895:n grams. There being the same number (n) of molecules in the 1000 cc. of Oxygen, each molecule of Oxygen weighs 1.429:n grams. Hence the ratio between the molecular masses of Hydrogen and Oxygen is

$$\frac{0.0895}{n} : \frac{1.429}{n}$$

or, n being cancelled,

$$0.0895 : 1.429$$

Now, 0.0895 and 1.429 are the weights of equal volumes of the two gases and also express their specific gravities or densities in relation to each other. Hence

The molecular masses of gases are proportional to their densities.

This is a very important deduction from the law of Avogadro and as densities of gases can be readily ascertained, the classical method of determining molecular mass is based upon it.

Normal volume or *molecular volume of gases.* As we will see later, the molecular mass of Hydrogen is 2. Further, a *gram-molecule* of a substance is that number of grams indicated by its molecular mass. A gram-molecule of Hydrogen is, then, two grams. One liter of this gas, at standard temperature and pressure, has a mass of 0.089578 grams: therefore two grams will measure

$$0.089578 : 1 :: 2 : x. \text{ or } 22.37 \text{ liters.}$$

Equal volumes of all gases contain the same number of molecules, therefore 22.37 liters of any gas must contain the same number; and the mass in grams of 22.37 liters of any gas measured at standard temperature and pressure, will represent its gram-molecule. Then to determine the molecular mass of any gaseous substance it is only necessary to determine the mass in grams of 22.37 liters. This is called the *normal volume* or *molecular volume.*

DALTON'S LAW.

Dalton's law relates to the tension of a gaseous mixture, and states: *the total tension of a gaseous mixture is equal to the sum of the tensions of the single gases (partial tensions) which they would exert when alone filling the same space.*

KINETIC THEORY OF GASES.

The properties of gases can best be explained by the following theory:

The molecules of gases are not in direct contact with one another, but are separated by intermolecular spaces. They are further in perpetual motion in straight lines and each having its own peculiar direction and velocity.

As a result of this incessant motion, collisions occur constantly, similar to those between pool balls. If we assume that molecules are elastic bodies it is evident that the direction and velocity will be changed after such collisions and will result in a zig-zag motion. They will also collide with the walls of the vessel in which the gas is contained and this is the cause of the tension exerted upon the container.

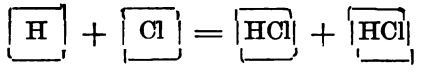
SECOND LAW of GAY-LUSSAC (*law of the chemical combination by volume*).

Gay-Lussac and Humboldt discovered that gaseous elements combine in certain proportions of volume as well as of weight. Thus when two gaseous elements combine, equal volumes of each may unite, or one volume of one with two, three, four, etc., volumes of the other; in other words *the volumes of the two combining gases bear a simple relation to each other.*

Gay-Lussac also found that *the volume of the gaseous compound formed maintains a simple relation to the volumes of the elementary gases entering into it.*

For a thorough study of this law and its experimental proof, consult A. von Hofmann's *Introduction to Modern Chemistry.*" Here are given results of a few experiments and the theories deduced.

1. Hydrochloric acid is a gas, a compound of two gaseous elements, Hydrogen and Chlorine. When subjected to quantitative analysis, it yields equal volumes of Hydrogen and Chlorine. Further, if equal volumes of the two are chemically united, two volumes of Hydrochloric acid gas result. If a single volume of a gas be symbolised by a square, these processss can be represented thus:



1 vol. of H + 1 vol. Cl = 2 vol. Hydrochloric acid

According to the law of Avagadro, equal volumes of all gases under like conditions of temperature and pressure, contain the same number of molecules; and therefore if the number of molecules in one volume of a gas be designated by n, it is seen that

1 n mol. of H + 1 n mol. of Cl = 2 n mol. of HCl.

and n cancelled shows that

1 mol. of Hydrogen + 1 mol. of Chlorine
= 2 mol. of Hydrochloric acid.

As each molecule of Hydrogen splits into two particles, we conclude that it consists of two *atoms*. If the atomic mass of Hydrogen be taken as one, the molecular mass will then be two. In like manner we arrive at the conclusion that a molecule of Chlorine must consist of two atoms, as it breaks down into two parts in the above reaction. Two atoms (one molecule) of Hydrogen and two atoms (one molecule) of Chlorine form two molecules of Hydrochloric acid; then one molecule of the compound contains one atom of Hydrogen and one atom of Chlorine. The application of the laws of Gay-Lussac and Avagadro permits an experimental determination of the number of atoms of each element contained in the molecule of a gaseous compound.

Representing the atoms by fractions of squares, the process may be illustrated as follows:

$$\boxed{H|H} + \boxed{Cl|Cl} = \boxed{H|Cl} + \boxed{H|Cl}$$

2. Water is a compound of Hydrogen and Oxygen and splits into these two elements when an electric current is passed through it, yielding two volumes of the former and one of the latter. If two volumes of Hydrogen and one of Oxygen be brought together and then chemically united, two volumes of water-steam will result.

2 vol. of H + 1 vol. of O = 2 vol. of water-steam.

The application of Avogadro's law shows it to be equally true that

2 mol. of H + 1 mol. of O = 2 mol. of water.

As one molecule of Oxygen breaks down into two particles in the formation of water, it evidently consists of two atoms; and as 4 atoms (2 molecules) of Hydrogen and 2 atoms (1 molecule) of Oxygen form 2 molecules of water, each molecule of water contains 2 atoms of Hydrogen and one of Oxygen.

3. If Ammonia is subjected to analysis, it is found to contain 1 volume of Nitrogen and 3 volumes of Hydrogen. Further experiments prove that these 4 volumes are contained in two volumes of Ammonia. Then

$$1 \text{ mol. of N} + 3 \text{ mol. of H} = 2 \text{ mol. of Ammonia.}$$

Hence 1 molecule of Nitrogen consists of two atoms and as three molecules of Hydrogen consist of 6 atoms, the molecule of Ammonia must contain 1 atom of Nitrogen and 3 atoms of Hydrogen.

It will be seen that in the cases of water and Ammonia a contraction occurs when the elements unite.

Other experiments give similar results and it may be stated that

1. The molecule of Hydrogen consists of two atoms. Hence its molecular mass is 2, because the atomic mass of Hydrogen is taken as the unit for measuring both the atomic and molecular masses of all other chemical substances.

2. The volume of one atom of Hydrogen is taken as unit for measuring volumes of other atoms and molecules and is called the *unit volume*. This is the volume of one atom-gram of Hydrogen, measured at 0° C. and 760 mm. pressure.

The *atom-gram* of an element is the number of grams indicated by its atomic mass. (In the case of Hydrogen, as we have seen, this is 1). It measures 11.185 liters.

3. As the molecule of Hydrogen consists of two atoms, the *molecular* volume of it, that is, the volume of one gram-molecule, will be equal to two unit volumes, or 22.37 liters.

Bi-volumic substances are those gaseous bodies whose gram-molecule measures, under standard conditions, just two unit volumes, or 22.37 liters. The molecule of Hydrogen is bivolumic.

4. The Avogadro's law requires that the molecular volume of all gaseous substances be equal, as like volumes of each, under like temperature and pressure, contain the same number of molecules. As chemical formulae represent molecules (see later), we arrive at the conclusion that

All molecules and formulae are bi-volumic.

5. As the molecular masses of gases are proportional to their densities (see page 50), and as the density of the atom of Hydrogen is taken as 1 and the molecular mass, therefore, two, it follows that

The molecular mass of any gas is obtained by multiplying its density by two; or

The density of a gas can be calculated by dividing its molecular mass by two.

The molecular mass of Carbon-dioxide is 44; therefore its density will be 22—that is, it weighs 22 times as much as the same volume of Hydrogen.

6. The molecules of all elements in the gaseous condition contain two atoms, with the exception of Sodium, Potassium, Zinc, Cadmium, Mercury and the Argon class which are monatomic, and Phosphorus and Arsenic, which are tetra-atomic.

Monatomic elements contain only *one* atom in their molecule.

Diatomic elements contain *two* atoms in their molecule.

Tetra-atomic elements contain four atoms in their molecule.

The *atomic* mass of a monatomic element is equal to its *molecular* mass; that of a diatomic to *half* its molecular mass; and that of a tetra-atomic element to *one-fourth* of it molecular mass.

As the symbols represent atoms, we deduce that

The symbol of a di-atomic element (in which the atom is one-half the molecule), represents one unit-volume—it is univolumic; that of a monatomic element (in which the atom is equal to the molecule) represents two unit-volumes—is bi-volumic; and that of a tetra-atomic element (in which the atom is equal to one-fourth of the molecule) represents half a unit-volume—is half-volumic.

The peculiar condition of Phosphorus and Arsenic.

These elements show peculiar volume conditions when they unite with other gaseous elements. The construction of the Hydrogen compound of Phosphorus may be represented as follows:

1 vol. of P + 6 vol. of H = 4 vol. of Phosphine.

A molecule of Phosphorus thus splits into 4 parts and consists therefore of 4 atoms. When 1 volume of Phosphorus unites with Hydrogen the resultant compound measures 4 volumes and not 2 volumes, as in the previous instances. In order to bring this experimental fact into harmony with the theory that all gaseous molecules measure two volumes, it is illustrated as follows:

½ vol. of P + 3 vol. of Hydrogen = 2 vol. of Phosphine

which contains one atom of Phosphorus and three atoms of Hydrogen in its molecule.

Arsenic behaves in identically the same manner.

The dissociation of the molecules of Sulphur and Iodine by heat. Sulphur, Chlorine, Bromine and Iodine exhibit extraordinary phenomena as the densities of their vapors are varied by changes of temperature. Sulphur vapor has a density of 96 at 500° C., while it has a density of 32 at 1200° C. Hence the molecular mass of Sulphur at 500° C. is 192, while at 1200° C. it is 64. Other experiments prove that its molecule at 1200° C. contains two atoms and the atomic mass is therefore 32. A molecule of Sulphur at 500° having a mass of 192 must then consist of six atoms. Thus the hexatomic molecule of Sulphur which exists at 500° C. breaks down into three di-atomic molecules when heated to 1200° C. and when cooled to 500° C. these reunite and form the hexatomic molecule again. In other words, the large molecule, when heated, *dissociates.*

The vapor-density of Iodine is 126 up to 900° C., implying a molecular mass of 254; but decreases with the further addition of heat until the temperature of 1500° C. is reached, here becoming stationary at 63, indicating a molecular mass of 126.

As further experiments prove that the molecule below 900° C. is di-atomic, its atomic mass is 126; therefore the molecule at 1500° C. is monatomic. Hence, when Iodine is heated from 900° C. to 1500 C. the di-atomic molecules dissociate and form mon-atomic ones.

CHAPTER IV.

EFFECT OF HEAT UPON BODIES.

Heat may produce four changes in matter:

1. *Chemical.*
2. *Change of volume.*
3. *Change in temperature.*
4. *Change from solid to liquid, or liquid to gas.*

CHEMICAL EFFECT OF HEAT.

Heat is the most powerful chemical agent. Chemical processes occur only within the limits of certain degrees of temperature. It appears that they do not take place below —125° C. Even such reactions as that of acids on litmus paper, of Sodium on alcohol, of Fluorine on glass, etc., do not take place below this. If the temperature is increased, the bodies begin to act, the energy of action increasing with the temperature until the maximum degree of activity is reached. Activity decreases with a further increase of temperature, until that degree is attained at which it ceases entirely.

Oxygen and Hydrogen do not act on each other at ordinary temperatures, but if the mixture is heated to about 200° C. a slow reaction commences, both gases partially combining to form water. If the temperature is gradually raised, rapidity of chemical action increases until at about 700° C. it is momentaneous, and the union of the gases occurs with a violent explosion. At over 1000° C. the affinity between the Hydrogen and

Oxygen begins to decrease again, water splitting up into its components gradually. The decomposition is half completed at 2500° C. and entirely at some higher degree as yet undetermined. Hence the chemical action between Oxygen and Hydrogen occurs only between 200° C. and about 4000° C., the maximum action being at about 700° C. In a mixture of Oxygen and Hydrogen at over 4000° C., both gases are entirely indifferent to each other and will only begin to act when cooled below 4000° C. the rapidity of action becoming greater the nearer the temperature approaches 700° C. The limits within which various bodies of different systems react on each other vary; but it is certain that such limits do exist for each individual system. Therefore we conclude that all compounds are decomposed into their elements and consequently that all molecules split into their atoms if subjected to sufficient heat. Heat is therefore one of the most powerful factors in decomposing chemical compounds. The example of the effect which a temperature of over 1000° C. has upon water, shows a very important chemical reaction which is called dissociation by heat.

Dissociation by heat is characterised by (a) the breaking down of a chemical compound into simpler components; (b) the gradual progress of decomposition, which is proportional to the temperature; (c) the ability of the compounds to reunite and form the original compound when cooled.

Those reactions cannot be called dissociation in which heat simply breaks down the substance without the components being able to reunite and reproduce the original substance when cooled.

Another example of dissociation is the effect of heat upon chalk (Calcium-carbonate), which gradually breaks down into lime (Calcium-oxide) and Carbon-dioxide; and when cooled these two will again form Calcium-carbonate.

Degree of dissociation or *fraction of dissociation* is the ratio of the weights of the dissociated substance to the total weight of the system. If 10 grams of Calcium-carbonate should be dissociated at a certain temperature, while 100 grams were originally taken, the degree of dissociation would be 1:10 or 10 percent.

Temperature of dissociation is that temperature at which the dissociation is half finished.

EXPANSION OF BODIES BY HEAT.

It is well known that nearly all bodies expand when heated and contract when cooled. An important exception is water below 4° C. which expands on being cooled. Above this temperature water behaves regularly and expands by heat. Hence water has its maximum density at 4°C., its specific gravity being there greater than at any other temperature. By reason of the expansion of bodies by heat, the capacity of volume measures varies with the temperature and it is necessary to have a standard degree at which to measure substances where accuracy is desired. In chemical apparatus, this is usually 15° C.

A practical application of the fact that the volume changes with the degree of heat is made in the thermometer.

The thermometer is an instrument used for measuring temperature. It consists of a long narrow glass tube, the bore of which is equal in diameter at all points. A bulb is blown at one end and this is filled with Mercury. Heat is then applied, causing the Mercury to boil and expel all air, and the tube is sealed. On cooling, the Mercury contracts, leaving a vacuum above it. The tube is then placed in melting ice and allowed to remain in it until the Mercury becomes stationary. The point to which it has fallen is marked as the *freezing point*.

This done, the bulb and tube are held in steam, just over the surface of boiling water, until stationary, when the *boiling point* is marked.

The distance between the two fixed points is then divided into degrees. Three different methods of dividing this space are extant.

1. *Centigrade* or *Celsius*. 100 degrees are marked off between the two points. The freezing point is zero or 0° C., the boiling point 100° C. This scale is used in all scientific work through-

out the world. Degrees of the same value are continued above and below the fixed points.

2. Reaumur. The freezing point in this scale is 0° and the boiling point is 80°. The intervening space is divided into 80 degrees, the portions of the tube below the freezing point and above the boiling point being divided into degrees of similar size.

3. Fahrenheit. This scale is generally used by English-speaking people. The space between boiling point and freezing point is divided into 180 degrees; but the freezing point is marked 32°, thus making the boiling point 212°. The portions of the tube above the boiling point and below the freezing are continued in similar degrees.

In all three systems temperature below zero is indicated by prefixing the number of degrees by the minus sign (—).

The relation between the three systems is

C 100 : R 80 : :F. 180.

or 5 : 4 : 9.

These numbers are the conversion numbers.

Value of a degree in another scale is the conversion number in the scale desired, divided by the conversion number in the scale given.

In order to convert degrees of one scale into another,

Multiply the degrees given by their values in the scale desired.

Subtract 32° from temperatures expressed in Fahrenheit before computing in another system, on account of the fact that zero in this scale is marked 32° the freezing point; and for a like reason, add 32° after computing from other systems into Fahrenheit.

EXAMPLES:

Convert 28° R. into C.

$$28 \times 5:4 = 35° \text{ C.}$$

Convert 55° C. into R.

$$55 \times 4 : 5 = 44° \text{ R.}$$

Convert 59° F. into C.

$$59 - 32 = 27$$
$$27 \times 5 : 9 = 15° \text{ C.}$$

Convert —13° F. into R.

$$-13 - 32 = -45$$
$$-45 \times 4 : 9 = -20° \text{ R.}$$

Convert 25° C. into F.

$$25 \times 9 : 5 = 45;$$
$$45 + 32 = 77° \text{ F.}$$

Convert —10° C. into F.

$$-10 \times 9 : 5 = -18;$$
$$-18 + 32 = 14° \text{ F.}$$

Absolute system. Another thermometer is constructed in which the interval between the freezing point and the boiling point is divided into 100 degrees as in the Centigrade thermometer, but the freezing point is marked 273°. This records absolute degrees, as discussed under the three states of matter, where we have seen that

$$T = t + 273$$
$$t = T - 273$$

A pyrometer is an instrument for measuring very high temperatures.

Sometimes, in place of Mercury, alcohol, Sodium and Potassium alloy, toluol, etc., are used.

Beckmann's differential thermometer. For many chemical operations we need an instrument which will record the difference between two temperatures regardless of the exact temperature of either one; these are called *differential thermometers.* They are often required to register variations of one-hundredth of a degree, therefore each single degree on the tube must

FIG. XII

occupy considerable space to allow of its division. To record between 6° C. and 60° C. a tube measuring several meters would be needed in the ordinary kind. As this is impractical, Beckmann has devised a thermometer of moderate size which indicates differences of not more than 5° and can be used in widely varying temperatures.

The upper end of the glass tube which contains the Mercury is connected with a glass vessel which acts as a reservoir. If the instrument is used to measure the difference between high temperatures, Mercury is shaken back into this reservoir; if low are to be measured, Mercury is shaken into the capillary tube again (fig.12).

(RAISE OF TEMPERATURE BY HEATING.

We must first distinguish between *temperature* and *quantity of heat.* A tumblerful of boiling water and a barrelful of it will each have a temperature of 100° C.—they are equally hot. The quantity of heat in each, however, is very different. The fuel necessary to heat the larger amount from 0° to 100°

must be very much more than that required to bring about the same change in the lesser quantity; and the barrelful will be able to heat a far greater quantity of cold substance to the same degree or the same amount to a much higher degree than is the tumblerful.

It is plain that temperature does not express the quantity of heat. This is relative to the quantity of the substance, and to measure it a fixed standard is necessary. The unit adopted by chemists is that amount of heat which will raise the temperature of one kilogram of water 1° C. and is called the *Calory*.

If the temperature of 30 kilograms of water of 0° C. be raised to 20° C., there have been expended 20 x 30 = 600 Calories of heat upon it—provided, of course, that no heat be lost during the operation.

Instruments for measuring the quantity of heat are called *calorimeters* and are of very varying construction. The fundamental principle of them all is that a heated body, when immersed in water, imparts heat to the liquid. The temperature increase and the volume of the water being known, the number of calories of heat can be calculated in the manner shown before.

SPECIFIC HEAT.

Mix together one kilogram of water of 10° C. and one of 60° C. and stir rapidly. Place a thermometer in the mixture and note the temperature—it will be seen to be exactly midway between the two temperatures or 35° C. The kilogram of water of 60° C. has therefore lost 25 degrees (25 Calories) while the kilogram of water of 10° C. has gained 25 degrees (25 Calories).

Now mix together one kilogram of water of 10° C. and one kilogram of oil of turpentine of 60° C. and note the temperature of the mixture as in the foregoing experiment; it will be found to be 24° C. In this instance, the temperature of the kilogram of turpentine has fallen 36°, while that of the kilogram of water has risen only 14 degrees. That is, the quantity of heat which raises the temperature of one kilogram of oil of turpentine 36 degrees will raise the temperature of the same amount of water

14 degrees. Thus the quantity of heat the oil of turpentine loses and the water gains is 14 calories.

The quantity of heat required to raise the temperature of one kilogram of different substances 1° C. is thus seen to differ in each case, a greater quantity of fuel being necessary to heat one kilogram of water from 1° to 100° than is needed to effect the same change in one kilogram of oil of turpentine; and on cooling, the water will part with much more heat than will the oil of turpentine.

The heat capacity of a body is that quantity of heat which is required to raise its temperature one degree Centigrade.

Specific heat is the relation of the heat capacity of a substance to the heat capacity of an equal weight of a standard substance. The standard being water, we may say: *the specific heat of a body is the relation of its heat capacity to that of an equal weight of water*; and further, as the heat capacity of one kilogram of water is one Calory, we may define that *specific heat of a body is the number of Calories necessary to raise the temperature of one kilogram of the substance* 1° C.

DETERMINATION OF SPECIFIC HEAT.

The specific heat of a body can be determined experimentally by weighing it, raising its temperature and exactly noting the degree, and then quickly immersing in water of known quantity and temperature. The immersed body gives up heat to the water until both have the same temperature. It can now easily be calculated how many degrees the substance lost and the water gained. The quantity of water being known, the number of Calories of heat gained by the water can be computed; it is evident that a like number of Calories were lost by the immersed body. Knowing the weight of this body and the Calories it has lost, is is easy to calculate how many Calories one kilogram of the body will lose when cooled 1° C.; and this is the specific heat of the body.

DULONG-PETIT LAW—ATOMIC HEAT. The Frenchmen Dulong and Petit were the first to compare the specific heats of the solid elements and were the discoverers of the following remarkable law: *if the specific heat of a solid element be multiplied by its atomic mass, the product is* 6.4 *or very close to that number.*

The specific heat of iron is 0.1138, its atomic mass 56 and the product of these numbers 6.37; the specific heat of Nickel is 0.1092, its atomic weight 58.8 and the product of the two 6.42; the specific heat of Lead is 0.0314, its atomic weight 205.03 and the product of these 6.4. The atomic weights of Iron, Lead and Nickel are 56, 205.3 and 58 respectively; if we suppose that there is in 56 kilograms of Iron n atoms, then in 205.3 kilograms of Lead there are also n atoms, and the same number in 58.8 kilograms of Nickel. As 6.4 Calories are necessary to raise the temperature of these n atoms of all solid elements 1° C., the quantity of heat required by single atoms to raise their temperature 1° C. is the same.

If the product of the atomic mass and the specific heat be called *atomic heat,* we arrive at a better expression of the Dulong-Petit law: *the atomic heats of all solid elements are the same, or nearly* 6.4.

CHANGE OF THE STATE OF A BODY BY HEAT.

If crushed ice or snow of—10° C. is placed in a beaker and slow heat carefully applied, the temperature rises until it reaches 0° C. and the ice begins to melt. The entire quantity of ice does not melt at once, quite a considerable time elapsing before the last piece disappears. During all this time a thermometer placed in the liquid will record a stationary temperature of 0° C. albeit the fire has burned steadily and has imparted heat to the ice. This heat has been absorbed in the melting process. The difference between ice of 0° and water of the same temperature is that the water has acquired heat not present in the ice and which neither the thermometer nor our sense of feeling can detect; this heat is the *latent heat of fusion,* and the temperature which the thermometer shows during the fusion is the *melting* or *fusion point* of the body.

Fusion is the melting of a body. *Refractory* bodies are those which will stand a high temperature without fusing.

The ice illustration is applicable to all substances which the exception of those substances which are chemically changed by heat; the only difference lying in the degree of temperature at which the fusion occurs. The melting point of ice is 0° C.;that of wax is about 64° C.;of Sulphur, 115° C.; of Tin, 230° C.; and of Lead 334° C.

It seems certain that every substance has a definite melting-point, although it has not been determined in all cases, it not being possible to attain a sufficiently high temperature.

Suppose the temperature of the melted ice is raised until it reaches 100° C., the water begins to boil—that is, it is converted into vapor. This is a gradual process, a long time being required before all is evaporated; and during all this time the thermometer registers a stationary temperature, 100° C., although the fire unceasingly imparts heat to the water. When all water is converted into steam, the temperature of this is also 100° C. Evidently heat imparted to water of 100° C. to convert it into steam of 100° C. is not perceptible to the thermometer or our sense of feeling and has been used to produce the conversion from one form to another. It is concealed in the steam produced.

This heat which a liquid absorbs when, by boiling, it changes to vapor without producing a change of temperature, is called *the latent heat of ebullition.*

Ebullition is the act of boiling. A substance whose boiling-point is so high that it cannot be reached by known means, or one which is decomposed by being boiled, is a *fixed substance*; while a substance which can be boiled without undergoing decomposition is *volatile.*

Pure substances have definite stationary boiling and melting points, while mixtures have not; and the purity of a body is sometimes judged by this fact.

If a vapor be cooled, it will resume the liquid form at the same degree of temperature at which it became gaseous; this is the

condensing point and is identical with the boiling point. Water boils at 100° C., forming steam; and steam condenses to water at 100° C. During this change from vapor to liquid the so-called latent heat of ebullition is set free and imparted to the container, the air and surrounding objects, causing a perceptible rise of temperature; this is called *condensation heat* and is equal in quantity to the latent heat of ebullition.

When a liquid is cooled it solidifies at the temperature at which it melted. This is called *freezing,* and the temperature at which it takes place is the *freezing- or solidification point.* This is identical with the melting point. By this change from liquid to solid, the latent heat of fusion is liberated and is perceptible to the senses; it is now called *solidification heat* and is equal to the latent heat of fusion.

Liquids do not always solidify on being cooled below their freezing point. Water, liquid Sulphur, Phosphorus, molten hyposulphite of Sodium and probably all other liquids can be retained in the liquid condition far below their freezing points by the process of *under-melting* or *under-cooling.*

This is effected by cooling the liquid without agitation and avoiding contact with anything that may contain a particle of the corresponding solid.

This indicates the tendency of the particles of a liquid to resist changes of condition, although the low temperature causes an unstable equilibrium.

Solidification of an undercooled liquid is immediately brought about if it is touched with a crystal of the same substance, no matter how minute; and the temperature is seen to rise exactly to that of the normal freezing point of the liquid. This is the only infallible method of solidification, although agitation and exposure will often bring it about.

Liquids are often converted into vapor at temperatures far below their boiling point. In this vaporisation latent heat is taken up. Solids also vaporise below their boiling points, as instanced by Camphor, Iodine, Napthalene and other solids vol-

atile at ordinary temperatures. Ice forms water-vapor below 0° C., and we know that wet clothes will dry, even though frozen.

Spontaneous vaporisation is the changing of liquids or solids to vapors at ordinary temperatures by exposure to air.

All bodies will absorb latent heat in order to change their state. This latent heat is taken from the surrounding objects and the more volatile a body is, the greater will be the cooling effect on its surroundings when it vaporises.

Ether produces a feeling of intense cold when poured upon the hand, by reason of the heat it absorbs in order to vaporise. If we place a test-tube containing water in a dish of ether and pass a current of air rapidly through the ether, the water will freeze. Easily-volatile liquids like ether, cymogen, liquified ammonia and liquified Carbon-dioxide can be used to prepare artificial ice or to produce low temperatures.

Many liquified gases solidify when permitted to vaporise. This is the case with Carbon-dioxide: evaporation of the first portion uses latent heat, which is taken up from the remainder of the liquid, cooling this portion sufficient to solidify it.

Cold produces insensibility of that part of the human body on which it acts. For this reason cold produced by the vaporisation of easily-volatile liquids (sprays of ether, rhigolene, ethyl chloride, etc) are used for local anesthesia in surgical operations.

Boiling point is affected by pressure; the greater the pressure the higher will be the boiling point and vice versa. Water has a lower boiling point on the mountain-tops, where the pressure is less, than at sea-level; thus varying pressure changes the boiling point.

The melting point is also affected by pressure, but in a far less degree than the boiling point. A remarkable phenomenon can be explained by this fact: reduction of pressure by means of an air-pump will often very materially reduce the boiling point of a substance, but will change its melting point very little; and

this results in bringing the melting and boiling points together or may even cause the boiling point to be theoretically lower than the melting point. In the latter case, a solid changes immediately to the gaseous condition, without melting, when heated. White Arsenic, calomel, and white precipitate do this.

In order to liquify Arsenic it would be necessary to heat under pressure, thus raising the boiling point without much changing the melting point. When the former is higher than the latter, Arsenic should be fusible.

The fact that heat affects the state of matter is applied in the following processes:

Evaporation—the conversion of a liquid into a vapor by heat. This method is employed to drive off a volatile liquid from a

FIG. XIII

substance less volatile. The solution to be evaporated is placed in an evaporating dish, and this is heated. The direct contact of heat may cause spurting, and the temperature at the end of the evaporation may rise so high that part of the substance it is desirous to retain unvolatilised may be driven off, or chemically decomposed.

To prevent this, a *bath* is used (fig. 13). This is a sort of kettle, in which water, oil, sand, or any suitable substance is heated, and having an open top on which the evaporating dish is placed. It is called a water-bath, oil-bath, sand-bath, etc., according to the filling. It is sometimes heated when empty, and is then

spoken of as a hot-air-bath; or, if filled with steam, as a steam-bath.

The temperature of the evaporating dish on a bath cannot rise higher than the boiling point of the liquid in the bath.

Desiccation—the process of drying. This is used to remove the liquid (usually water) which adheres to solid bodies. Dessication may be performed *with* or *without* heat.

(a). *Desiccation with heat* is accomplished in *drying ovens.* These are boxes made from copper and provided with a door and having shelves inside. There are two tubular openings at the top, one being intended to allow the steam to escape, the other to carry a thermometer. The door, in its lower part, has several small openings which admit a current of fresh air and thus facilitate drying.

(b). *Desiccation without heat.* We have seen that a liquid can evaporate at ordinary temperatures, and many substances can be dried by exposure to air

FIG. XIV

This can be quickly done by placing the wet substance in a chamber that is kept entirely and continually dry. To maintain this state of dryness, Sulphuric acid, Calcium-chloride, Phosphorus-pentoxide and other substances which are able to absorb moisture from air are used. An apparatus for drying solids in this manner is a *desiccator.* It is a glass vessel of the shape shown in fig14. The lower part contains Sulphuric acid or other desiccating agent; in the upper part is a wire triangle on which a dish, containing the substance to be dried, is placed. The apparatus is then closed by a tight-fitting cover, the margin of which is smeared with vaseline to make the closure perfect.

Distillation—the process of vaporising a liquid and then condensing the vapors. Bodies which volatilise at different temperatures may be separated by this method. In *evaporation* the vapors are allowed to escape; while in *distillation* they are cooled and collected.

Two kinds of distillation are to be distinguished:

(a). Common *distillation*—that used where the boiling points of two substances differ so widely that one may be regarded as a fixed substance in comparison with the other. The vapors obtained by heating such a mixture are those of the liquid with the lower boiling point only.

Various kinds of apparatus are used to carry on distillation, the most simple form being that of the *retort and receiver.*

In operation, the retort is filled about half-full with the mixture to be distilled, and its neck inserted into the neck of

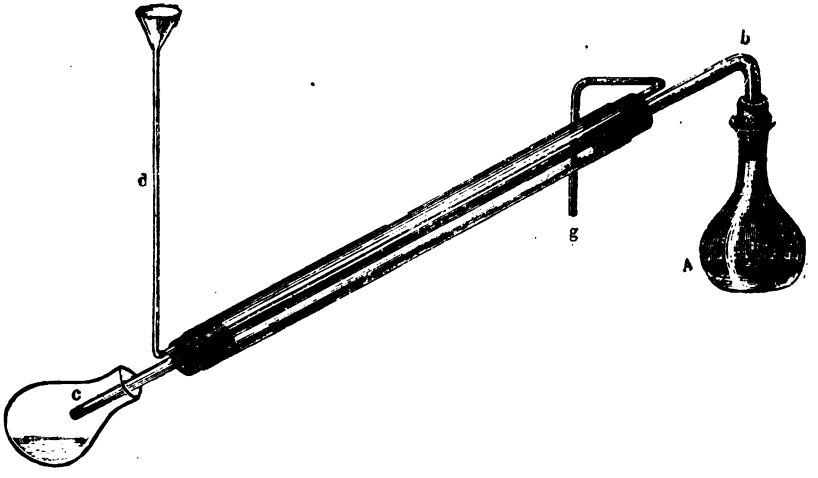


FIG. XV

the receiver. Heat is applied to the retort, usually by means of a bath. This causes the more volatile liquid to vaporise and pass into the receiver, where it is condensed by the cold transmitted from the air. To assist in condensation, water is often allowed to fall on the receiver. For liquids whose boiling points (condensation points) are very low, other means are needed to condense their vapors. Here a *condenser is employed*; the one most used being the *Liebig's condenser.* (fig.15.) This is usually

made of glass and consists of a long tube which conducts the vapors from the retort, jacketed by a wider one through which passes a constant stream of cold water flowing in an opposite direction to that of the vapor. This keeps the tube cool all the time and the vapors quickly condense.

(b). *Fractional distillation.* This is a process used to separate volatile liquids of different boiling points. It is similar to ordinary distillation, except that the process is interrupted at different temperatures to obtain distillates, which contain varying proportions of each liquid, according to the degree of heat applied.

If a mixture of alcohol, having a boiling point of 78° C. and water, whose boiling point is 100° C. is heated, vapors of both ingredients are given off (all volatile liquids evaporate below their boiling point); but there is a larger percentage of alcohol vapors than of water vapors. Therefore, if the distillates be periodically removed, the first ones will contain the greatest percentage of alcohol; each subsequent one containing a smaller proportion. It follows that the percentage of water in the residue increases steadily as the distillation progresses, and the boiling point of the residue will become higher.

The fractional distillation of an alcohol-and-water mixture is made as follows:

The mixture is placed in a retort in the tubulature of which a thermometer is fastened to record the temperature during the operation. Distillation is started and the temperature rises; heat is applied until the thermometer records 83° C., and the receiver now contains the distillate between 78° C. and 83° C. The receiver is now changed and the liquid which distils between 83° C. and 88° C. is collected. Again a fresh receiver is attached and the temperature allowed to rise to 93° C. and so on by increments of 5° up to 100° C. We thus obtain these distillation fractions:

I. 78° to 83° contains the largest proportion of alcohol.
II. 83° to 88° contains less alcohol than I.
III. 88° to 93° contains less alcohol than II.

IV. 93° to 98 contains less alcohol than III.
V. 98° to 100° contains nearly pure water.

Distillate number I. is placed in a retort and again heated. When the temperature has reached 83° C. some liquid still remains undistilled; consequently the distillate now obtained contains a greater percentage of alcohol than fraction I. did. The receiver is changed, fraction II. added to the residue in the retort, and the temperature raised to 88° C. The liquid does not all vaporise, showing that this distillate is richer in alcohol than distillate II. All the primary distillates are subjected to this redistillation. The later distillates evidently contain more alcohol than the primary and if the process is repeated a complete separation of the alcohol and water is finally attained.

Fractional distillation is much used in industry—in the manufacture of alcohol, in the separation of benzine, gasoline and the like from American petroleum and in many other ways.

It is often desirable to heat volatile substances together without loss by evaporation. This is done in the following manner:

1. If it is required to raise the temperature to the boilingpoint only, the *upright* or *reflux condenser* can be utilised. A flask containing the liquid is closed by a cork through which the inner tube of a Liebig's condenser is inserted in an air-tight manner, the condenser standing upright. A stream of cold water is passed through the condenser-jacket, and the inner tube through which the vapor from the heated flask ascends is cooled and the vapors thus condensed flow back into the flask. This eliminates all loss of liquid by evaporation.

2. If it is desired to raise the temperature *above* the boiling point of the liquid, evaporation is prevented by pressure, which increases the boiling point. In order to heat small quantities in this manner, they are sealed in thick-walled glass tubes and these heated in a suitable furnace constructed for the purpose. In factories, *autoclaves* or *digesters* are used; they are strong boilers having steam gauge and safety valve.

Sublimation is the process of vaporising a solid substance and cooling the vapor below its solidification or freezing point.

The melting point of camphor is 175° C., and when camphor is heated above 205° C. it vaporises. If now the vapors are cooled below 175° C., they solidify.

Sublimation is used for the separation of solid substances of which one is volatile. The process is well illustrated when a few crystals of Iodine are heated in a dry test-tube; violet vapors of Iodine are seen to rise, which solidify in the cooler part of the tube, forming a black sublimate.

Sometimes is is desirable to evaporate, distil or sublime substances at temperatures below their regular boiling points.

The law that decrease of pressure lowers the boiling point of a substance is applied and the apparatus used is the *vacuum apparatus.* The most simple form consists of a retort, a condenser and a receiver, all connected in an air-tight manner. The receiver is tubulated, and is connected with a suction pump, by means of which the air is withdrawn from the apparatus.

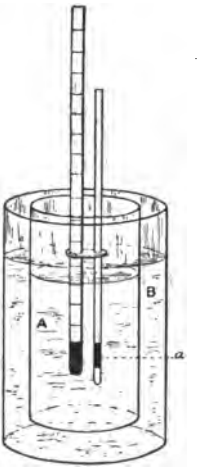


FIG. XVI

DETERMINATION OF THE MELTING POINT.

This is of importance to chemists and is used in identification and as a test for purity. Wax, if pure, melts at 64° C.; should the melting point of a sample vary from this, its impurity is evident. Below are three methods for the determination of the melting point:

1. *Common method.* The substance is finely powdered and put into a test tube, and a thermometer placed with the bulb in the powder. This tube is heated and the temperature raised until fusion begins. The thermometer now records a stationary degree of heat until all is melted and this is the *melting point.*

This method is exact, but cannot always be employed as large quantities are needed for its performance.

2. *Capillary tube method.* This method is based on the fact that many substances, when solid, are opaque, but transparent when liquified. A little of the powdered solid is put in a capillary tube, a (fig. 16), sealed at one end in such a manner that the powder forms a layer in the sealed end. This tube and an accurate thermometer are placed side by side in a heater so that both are subjected to the same temperature. The heater A is then filled with a liquid having a higher boiling point than the approximate melting point of the substance. To secure equal distribution of heat, A is placed within B, which is filled with the same liquid. Heat is carefully applied, and the point at which the substance becomes transparent noted. It can then be allowed to cool, and the freezing point determined.

3. *Method of undercooling* (*Beckmann's method*). We have seen that liquids at rest and not in contact with air, can be cooled below their melting points without being solidified; and that the introduction of a crystal of the solid in solution causes crystallisation and a rise in temperature to the normal freezing point. This point can be determined with wonderful exactitude by means of Beckmann's apparatus (fig. 17).

A is a strong test-tube with a side tube B, which can be opened and closed by the stopper C. The liquid of which the freezing point is desired is introduced through B into A, which is then closed by a cork carrying a thermometer D, graduated to tenths of a degree. A stirrer, E, of platinum wire passes through the cork to the bottom of the tube by means of which the substance can be agitated. The test-tube A passes through a hole in the cork and sets into the large test-tube G, being thus surrounded with air. The whole is immersed into the beaker, H, in which there is a cooling fluid having a temperature

slightly below the freezing point of the substance to be examined.

The tube G forms an air-jacket between the tube A and the cooling mixture in the beaker, causing a uniform cooling of A.

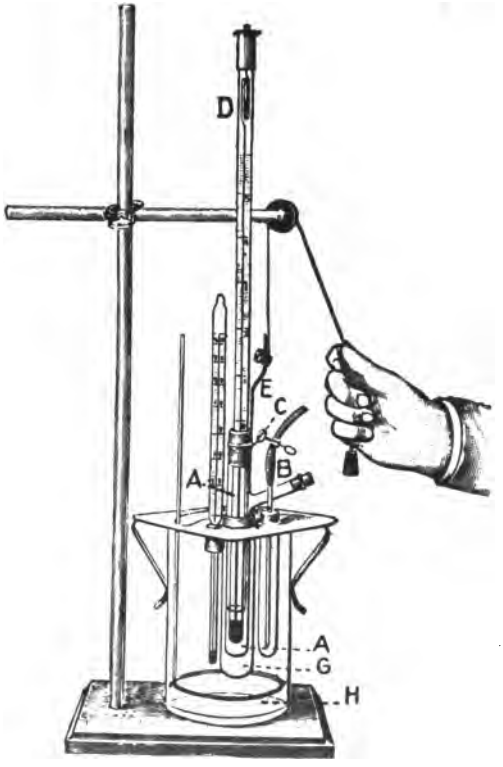


FIG. XVII

In order to determine the freezing point, about 20 grams of the liquid is placed in the tube A and undercooled. Now by agitation or the introduction of a piece of the corresponding solid into the liquid, solidification is accomplished. The thermometer records a stationary temperature, which is the freezing

point. This method, like 1, is very accurate; but a considerable portion of the liquid is needed.

DETERMINATION OF THE BOILING POINT.

For this purpose, flasks are used like those shown in fig. 18. This has a tube projecting from the long neck. A thermometer

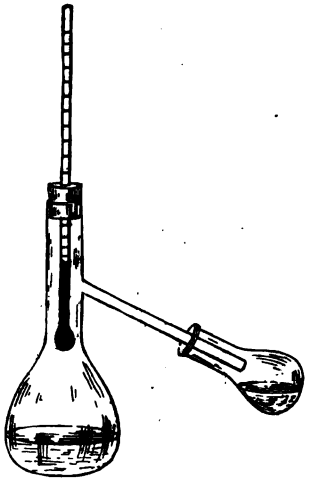


FIG. XVIII

passes through the cork, its bulb being above the point where the surface of the liquid reaches, but below the side-tube. Heat is applied until the boiling point is reached and the vapors pass out through the side-tube. In doing so, they come in contact with the bulb of the thermometer; and as they have the same temperature as the boiling point, this can be easily read off.

CHAPTER V.

SOLUTION.

A solution is any mixture which is entirely homogeneous. In a solution the constituents are distributed with perfect uniformity; and the proportions of the quantities of all constituents are the same throughout. It is impossible to distinguish, even microscopically, between particles of one of the constituents and particles of another. A solution is generally considered as a *liquid,* in which a solid, liquid or gas is dissolved; but this is not scientifically correct, the liquid condition not being essential. We will deal first with those solutions obtained by dissolving a solid in a liquid.

A solvent is a liquid used in making a solution. Water, alcohol, ether and benzol are the most used solvents. There are two kinds of solutions, *simple* and *chemical.*

A CHEMICAL SOLUTION is one in which the identities of the solvent and dissolved substance are so changed that they can no longer be recognised; and, if the solution is evaporated, a different substance with new properties is obtained. A chemical solution also takes place in certain definite weight-proportions of the constituents. An example of chemical solution is that of a metal in an acid.

A SIMPLE SOLUTION is one which can be made in varying weight-proportions of the constituents; further, these are not chemically changed and, upon evaporation, the original solid is regained. We will treat here of simple solutions only.

The quantity of a solid which can be dissolved by a given quantity of a liquid is limited. We therefore distinguish between:

1. *Saturated solutions*—those which contain as much of the solid as they can dissolve.

2. *Unsaturated solutions*—those which are capable of dissolving still more of the solid.

The solubility of a substance is expressed in numbers which state the relation of the weight of the dissolved solid to that of the solvent in a saturated solution. The solubility of salt in water is 1:3—that is, one gram of salt with three grams of water forms a saturated solution.

Solubility depends on temperature. It is generally increased by addition of heat. A solution, saturated at a certain temperature, becomes unsaturated when heated to a higher degree. In some few instances a substance is more soluble at low than at higher temperatures. Lime, gypsum. Calcium-citrate and all gases are more readily soluble in cold than in hot water.

As a definite limit of solubility exists for each degree, a standard temperature must be accepted at which to state solubilities; this is usually 15° C., but the U. S. P. gives 25° C.

If a hot saturated solution of a solid that is more soluble at high temperatures is cooled, the solvent cannot longer retain all the solid in solution and the surplus gradually separates and forms crystals. With solutions of substances which are more soluble in cold than in hot, the reverse is the case; when heated, they will not retain all the dissolved substance, but the excess will be deposited as the temperature rises. This is seen in limewater, which gets cloudy on heating.

Hygroscopic bodies are those which absorb water vapors from the air; they may be solid (Calcium-chloride), liquid (Sulphuric acid) or gaseous (Hydrogen-chloride).

Deliquescent bodies are those which absorb water vapor from the air and dissolve in this. Examples are lye, Calcium-chloride, Zinc-chloride and Potassium-carbonate.

In certain instances, a hot saturated solution of a solid more soluble at high temperatures, may be cooled far below the ordinary temperature without crystallising if covered and kept still, A solution of this kind is a *supersaturated solution.* If a crystal of the solid contained is put in, solidification of the whole takes place.

When a solid is dissolved in a liquid of the same temperature, the solution formed shows a degree differing from this. Some solids, when dissolved, produce a temperature *decrease, as* in the case of saltpetre in water; others an increase, as in the case of caustic potash in water. To restore the solution to the same temperature as the constituents previously had, it is necessary to add or detract a certain number of Calories of heat; this is the *heat of solution.*

When the temperature *rises* during the process this is *positive* and when it *falls* it is *negative.*

All gases produce positive solution heat; that is, the tempera ture always rises when a gas is dissolved in a liquid.

When two liquids are mixed, temperature changes also occur. Alcohol and water become warmer when mixed; while Carbon-di-sulphide and alcohol suffer a decrease of temperature when mixed.

Even when a concentrated solution of a solid is diluted with more of the solvent, temperature changes occur. In order to restore the original temperature, it is necessary to withdraw or add heat, and this is the *heat of dilution.* It is positive or negative according to whether the temperature is raised or lowered.

Freezing mixtures are those mixtures of solid and solvent which cause by their solution so great a reduction of temperature that, if a vessel containing a liquid is immersed in them, the contents are frozen. A mixture of 8 parts powdered Glaub-

er's salt and 5 parts commercial Hydrochloric acid produces a lowering of 27.8° C.

Salt with crushed ice also produces great reduction of temperature. In this instance the effect is produced

(a) by the melting of the ice (latent heat of fusion); and
(b). by the negative solution heat developed by the mixture.

FREEZING of SOLUTIONS.

The freezing point of a solution is lower than that of the pure solvent.

Depression of the freezing point is the difference between the freezing point of the solution and that of the pure solvent.

Water freezes at 0° C., seawater at about —2° C.; hence the freezing point depression of seawater is 2° C.

BLAGDEN'S LAW.

The depression of the freezing point is proportional to the concentration of the solution; that is, to the percentage of the dissolved substance contained.

A 4 percent solution, then, will have a freezing point depression twice as great as a 2 percent one of the same solid in the same solvent.

This law does not hold good with aqueous solutions of acids, bases or salts (see electrolytic dissociation).

RAOULT'S LAW.

If a gram-molecule of each of several different substances is dissolved in an equal quantity of water, the depression of the freezing point is alike in every case.

This law does not hold good with aqueous solutions of acids, bases or salts (see electrolytic dissociation).

Molecular depression of the freezing point of a solvent is the depression produced by any molecule gram when dissolved in 100 cc. of the solvent. That of water is 18.6° C., of acetic acid 39° C. and of benzol 49° C.

The determination of the freezing point depression is of importance, and is used to ascertain molecular mass and osmotic pressure. It is also used in medicine under the name of

Cryoscopy. As the solvent contained in the body-fluids is invariably water, the cryoscopy of urine, blood, etc., is the determination of the difference between the freezing point of water (0° C.) and that of the fluid under consideration. The determination is accomplished with a Beckmann's apparatus (which see), and a Beckmann's differential thermometer. The method has been previously described. The freezing point of the pure solvent is first noted, then that of the solution. The difference is the freezing point depression.

When a diluted solution is partially frozen, the solid substance which separates consists of the solvent only, and contains none of the dissolved substance.

The ice formed on the ocean is pure and contains no salt, unless a small amount of the seawater be *mechanically* enclosed within small cavities in the ice. Water, colored by a dye, forms colorless ice.

This law may be applied:

1. For the preparation of pure water by partially freezing impure water. The ice formed is melted, and then again partially frozen and the process repeated several times. This yields the purest water obtainable.

2. For concentration of diluted solutions. These may be partially frozen and the ice removed, leaving a more concentrated residue.

This fact should have an important bearing on industries conducted in countries where the winters are very cold, as a saving of much fuel otherwise necessary for evaporation can be accomplished.

If a diluted solution is partially frozen time after time and the ice removed after each cooling, the remaining liquid, becoming more concentrated, will have a lower freezing point; the solubility of the solid also decreases every time the temperature

is lowered, and a point is finally reached where the solution is saturated at is freezing point. If further cooled, the liquid will freeze and the dissolved substance will crystallise. This results in the formation of a solid mixture of frozen water and crystals of the dissolved substance, a *kryo-hydrate,* which is characterised by having a definite composition and a constant melting point. In this respect it is like a true chemical compound.

A kryo-hydrate can be made by mixing 33 parts of common salt with 100 parts of water and cooling to —21.3° C.

BOILING of SOLUTIONS.

The boiling point of a solution is higher than that of the pure solvent.

The elevation of the boiling point is the difference between the boiling point of the solution and that of the pure solvent.

WUELNER'S LAW.

The elevation of the boiling point of a solution is proportional to the concentration; that is,to the percentage of the dissolved substance. In a 6 percent solution it will be twice as great as in a 3 percent solution of the same solid in the same solvent.

This law does not hold good with aqueous solutions of acids, bases or salts (see electrolytic dissociation).

RAOULT-BECKMANN LAW.

When a gram-molecule of any substance is dissolved in a fixed quantity of the same solvent, the boiling point is equally elevated in all instances.

Thus one gram-molecule of anthracene and one of napthalene each dissolved in 1000 grams of benzol, elevate the boiling point alike 2.67 degrees.

This law does not hold good with aqueous solutions of acids, bases or salts (*see electrolytic dissociation*).

Molecular elevation of the boiling point is that produced by one gram molecule of any substance in 100 grams of the solvent. That of benzol is 26.7° C., Chloroform 36.6° C., water, 5.2 C. This is applied in the determination of the molecular mass.

Solubility of a solid in two immiscible solvents. In many instances different solvents will not mix together, but separate in the manner of oil and water, the lighter floating on the others.

If a solid is shaken with a mixture of this kind, in each of the components of which it is soluble, it will be taken up by each; and if equal volumes of two solvents are employed, the solid divides between them in a certain proportion, which is its *partition coefficient* in regard to the two solvents. This is not dependent upon the amount of the solid, but upon the temperature. For example, if any quantity of Iodine is shaken with a mixture of equal parts of water and Carbon-disulphide at 15° C., the quantity dissolved by the Carbon-disulphide is 410 times as great as that dissolved by the water: hence the partition-coefficient of Iodine at 15° C. in regard to water and Carbon-disulphide is 410.

DIFFUSION and OSMOSIS.

If a concentrated solution of any substance is poured into a bottle and then the pure solvent very carefully added, the solvent, having a lower specific gravity, will form a layer on the heavier liquid. Should the bottle be now placed aside, avoiding all shaking, the liquids will become mixed in time. This is the process of *diffusion.*

The velocity of diffusion is variable. Substances which are crystallisable diffuse rapidly; while substances like gum and glue, which do not crystallise, have a very slow rate of diffusion.

Colloids are bodies having a very slow rate of diffusion.

Crystalloids are bodies which diffuse rapidly.

If the experiment just described is repeated, with the addition of a porous membrane (pig's bladder, parchment paper), where

the solution and the solvent come in contact, is is seen that a solution of a crystalloid mixes with the solvent through the membrane; while a colloid does not mix and is unable to pass through the membrane. This phenomenon is called

Osmosis. It continues until the concentration of the solution is the same on both sides of the membrane. It may be used to separate crystalloids from colloids. If a solution of salt in water is mixed with a solution of a gum, the mixture enclosed in an animal bladder, and the whole suspended in water, the salt, being a crystalloid, will pass through the bladder and mix with the outside water; while the gum, being a colloid, cannot pass through and will remain inside the bladder. Constant renewal of the outside water will eventually remove all salt.

Dialysis is the separation of crystalloids from colloids by means of osmosis.

A dialyser is an instrument used to separate crystalloids from colloids by means of osmosis. It consists of a ring with one end covered by parchment paper, in which the solution to be dialysed is placed, and the whole suspended in a vessel filled with the pure solvent (fig. 19).

The usual osmotic experiments are made with such membranes as those mentioned, which allow osmosis from either side as the following example shows:

When a solution of Copper-sulphate, which is blue in color, is put into a tube and this closed by parchment and suspended in water, the liquid is seen to rise in the tube, thus water has passed through the membrane; at the same time the water in the dish assumes a blue color, showing that some Copper-sulphate passed out from the tube. The membrane in this instance is evidently permeable to both substances.

Semi-permeable membranes only admit of the passage of the solvent and not of the dissolved body.

There are several which are permeable to water but not to a number of crystalloids; the most important of these are:

Precipation membranes are formed by floating one liquid on another which is heavier and with which it forms a precipitate at the zone of contact. Membranes are thus formed which are permeable to water, but not to many crystalloids. The form most used is the Copper-ferrocyanide membrane, made by adding a solution of Copper-sulphate to one of Potassium-ferrocyanide.

Pfeffer was the first to make practical experiments with these membranes, and he constructed the *Pfeffer's cell.* This consists

FIG. XIX

of a porous clay cell which is filled with a solution of Potassium-ferro-cyanide and placed in a solution of Copper-sulphate until the pores of the cell are completely filled with a precipitate of Copper-ferro-cyanide, which makes the cell semi-permeable.

In operation, the cell is well-washed and then completely filled with a solution of the substance whose properties are to be investigated. The cell is closed by a stopper carrying a tube extending out from the instrument. The whole is then suspended in pure water and the liquid is seen to gradually rise in the

KINETIC THEORY OF SOLUTIONS.

By reason of the above analogy between gas laws and solution laws, we conclude that the molecules of a dissolved substance are in motion like those of a gas; that is, in straight lines until they collide with fellow molecules or with their container.

Isomotic or *isotonic solutions* are those with the same osmotic pressure. In physiology, an *isotonic* solution is one that has the same osmotic pressure as the blood-serum; a *hyp-isotonic* solution one that has a lower and a *hyper-isotonic* solution one that has a higher osmotic pressure than blood-serum.

A *physiological* or *normal salt solution* is a solution of Sodium-chloride in water which is isotonic with the bloodserum. For human blood, this is a 0.9 percent solution.

The depression of the freezing point and the elevation of the boiling point of diluted solutions also bear certain relations to the osmotic pressure. For instance, the molecular depression of the freezing point of water is 18.6° C. As an aqueous solution having a grammolecule of any dissolved solid in a liter exerts an osmotic pressure of 22.37 atmospheres, we observe that a depression of the freezing point of 18.6° C. is equal to 22.37 atmospheres of osmotic pressure. Hence the depression of the freezing point or the elevation of the boiling point may be used to calculate the osmotic pressure.

Semi-permeable membranes are of frequent occurrence in nature in plant and animal life, but are of microscopic size.

The cell of the organism is usually surrounded by a membrane of this description, and this allows the passage of water but not of many crystalloids. If a cell is placed in a solution having a greater osmotic pressure than that within the cell, it will contract by reason of the passage of water out of it in an attempt to equalise the concentration; but as the cell-contents continue to contract they reach a point where they separate from the wall, which has reached the limits of its elas-

ticity and can no longer accomodate itself to the lessened bulk of its contents. This is *plasmolysis.*

If the cell is placed in a liquid of lesser osmotic pressure than that existing within the cell, it will be expanded in the attempt to equalise the concentration of the two solutions. The cell will increase in size to the limits of the elasticity of the membrane, and will finally burst when it can no longer resist the internal pressure. This is *plasmoptysis.*

SOLUTIONS of LIQUIDS and GASES in LIQUIDS.

It is found that solutions of liquids in liquids, and of gases in liquids behave similarly to those of solids in liquids.

The solubility of a gas in a liquid is not usually expressed in terms of weight, but is stated as the number of cubic centimeters of the gas which one cubic centimeter of the liquid will dissolve; and because the volume of all gases is governed by temperature and pressure, certain standard conditions must be observed. These are generally accepted as 0° C. and 760 mm. pressure and, when not otherwise stated, these conditions are understood.

The absorption coefficient of a gas in a given liquid is the number of volumes of the gas soluble in one volume of the liquid.

When a gas dissolves in a liquid, heat is always produced. Then *all gases have positive solution heats.*

The absorption co-efficient of a gas in a liquid decreases with increased temperature and gases are less soluble in liquids when heated. Change of pressure also affects the solubility, which is increased by additional pressure.

HENRY'S LAW.

The mass of a gas which is soluble in a definite quantity of a liquid is proportional to the pressure; or

Tte absorption coefficient of a gas in a liquid is proportional to the pressure.

If one liter of a liquid dissolves one liter of a gas under standard conditions, it will dissolve three liters if the pressure be trebled and the temperature kept stationary.

DALTON'S LAW of the SOLUBILITY of GASES.

The quantity of each gas absorbed by a liquid from a mixture of gases does not depend on the total pressure (tension) of all the gases but only on the partial tension of the individual gas.

In order to increase the solubility of Carbon-dioxide in water it is useless to press any other gas onto the surface of the liquid, but it is necessary to exert the pressure on the particular gas which is to be made more soluble—in this case, Carbondioxide

In order to expel a gas from its solution, the following methods are used:

1. Decrease of pressure. When a bottle of soda water is opened, the pressure is released and the gas can be seen escaping from the water.

2. Exposure to air. If the dissolved gas is not contained in the air, it will escape because there is no partial tension to oppose its liberation.

3. By the addition of heat.

4. By freezing. Water, which usually contains absorbed air, gives this up when frozen. When silver is melted in air, it absorbs Oxygen in large quantities; but when it solidifies again, this is driven off, causing what is known as the 'spitting' of Silver.

5. By agitation.

6. By solution of another substance in the gas solution. Seltzer water effervesces much more readily if sugar is put in.

Effervescence is the sudden escape of a gas from a liquid. It is accompanied by the formation of bubbles.

SOLUTIONS of GASES in SOLIDS.

Solids also absorb gases, especially if porous—like charcoal. The maximum quantity absorbed depends upon the pressure and temperature; increase of pressure allows of more, while rise of temperature lessens the amount. If the gas absorbed is Oxygen and the solid body one that burns in this gas, it may happen that the heat produced will be sufficient to reach the temperature of ignition and the solid is set on fire. Bodies of this nature are called *pyrophorous bodies,* and comprise Iron-powder (freshly reduced by Hydrogen), Potassium-monosulphide (prepared by glowing Potassium-sulphate with lamp-black), etc. Freshly prepared charcoal often ignites spontaneously. Even heavy solids like Platinum and Palladium will absorb a considerable bulk of Hydrogen when heated in a stream of it. They retain some of the absorbed gas on cooling. It is found that Palladium absorbs 643 volumes of Hydrogen at 95° C. This property of solids by reason of which they absorb and retain gases is called *occlusion.*

The occlusion of gases is permitted by the fact that all metals, even the most dense, are more or less porous ; the gas passes into these invisible pores and is there retained by the surface attraction of the solid body. Increased temperature has a twofold effect upon this process. It causes the metal to expand—the pores thus becoming larger and the surface exposed greater, favoring an increased occlusion; on the other hand, heat increases the kinetic energy of the moving molecules of the gas and they are thus aided to escape from the attraction-sphere of the molecules of the metal, tending to decrease occlusion. At very high temperatures the pores of the metal become so large that gas molecules can penetrate through the metal. Many metals allow the passage of gas at high temperature in this manner.

CHAPTER VI.

CRYSTALLOGRAPHY.

Solid bodies are all either *crystalised* or *amorphous* (without crystalline form). A *crystal* is a solid having regular geometrical form and having plane surfaces, called faces. Where two of these intersect, a straight edge is necessarily formed; and where more than two edges met, corners are formed. The edges form angles, the vertex of which is a corner. Their magnitude is characteristic of the individual crystal. The faces, edges and corners are arranged symmetrically around imaginary lines, the *axes* of the crystal.

The majority of crystals can be divided into two symmetrical parts by a plane extended through the crystal; this is called the *plane of symmetry* of the crystal.

Every face, edge, corner or angle of a symmetrical crystal has a corresponding opposite face, edge, corner or angle equal in shape, magnitude and relative position.

An axis is an imaginary line extending through the interior of the crystal and connecting the center of two opposite symmetrical edges, corners, etc. One is placed vertically and is called the vertical axis; the others intersect this. The various magnitudes of the angles at which the axes intersect each other in different crystals are characteristic in each case, and they are classified accordingly.

THE SYSTEMS of CRYSTALS.

There are two general divisions of these:

I. Those having three axes.
II. Those having four axes.

The first class has two subdivisions:

(a). Those in which all three axes intersect each other at right angles—*the orthometric systems.*

(b). Those in which not all three axes intersect each other at right angles—*the klinometric systems.*

The six systems may be arranged as follows.

CLASS I.
Those with three axes.

ORTHOMETRIC— The three axes intersect each other at right angles.

(a). *Regular, tesseral or monometric system*—having all three axes of the same length.

(b). *Tetragonal, quadratic or di-metric system*—having only two axes of the same length.

(c). *Rhombic or tri-metric system*—having all three axes of different length.

KLINOMETRIC—having three axes which do not all intersect at right angles.

(a). *Monoklinic system*—having three unequal axes, two of which intersect at oblique angles; the third forming right angles with the others.

(b). *Triklinic, klino-rhombic or asymmetric system*—having all three unequal axes intersect in angles which are not right angles.

CLASS II.
Those with four axes.

Hexagonal or *Rhombohedral system*—having three axes of equal length in the same plane and intersecting each other at angles of 60°; the fourth axis (the vertical one) is different in length to the others and stands perpendicular to them.

The study of the different forms of crystals is called crystallography. This book will not treat of the crystallography of each of the systems, but will touch only on a few of the more common forms whose names are often met with.

Regular octahedron, consisting of six corners, twelve edges and eight faces which are equilateral triangles.

Cube, consisting of eight corners, twelve edges and six faces which are squares.

Prism. The lateral faces are parallelograms, while the upper and lower faces (called bases) are equal polygons, the borders of which are parallel and of equal length.

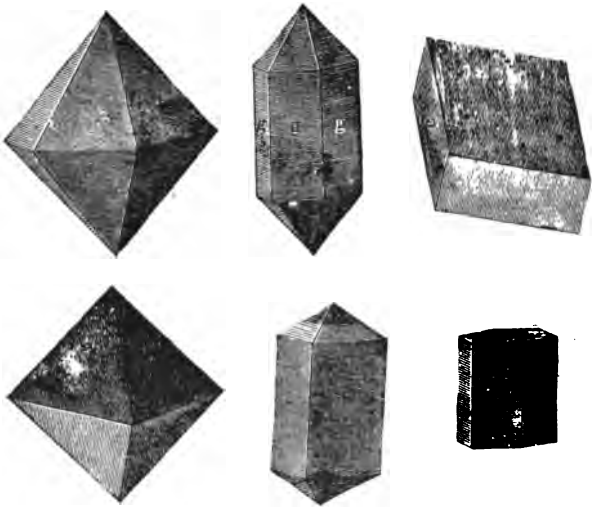


FIG. XX

Pyramid consisting of a base which is a polygon, the other faces being triangles and meeting at a point called the vertex. Pyramids generally combine in such a manner that they have a common base; or a prism, having an equal base, is inserted between the two.

Tabular crystals are flat plates.

Laminar crystals are formed of thin layers.

Acicular crystals are needle-shaped.

Figure 20 illustrates a few forms of crystals.

When a solid substance does not show crystalline form under the microscope, it is said to be amorphous. Glue, rubber, albumen, etc are amorphous. Not only does the form of these differ from crystallised bodies, but other physical properties also.

Hard amorphous bodies break unevenly in all directions, while crystals split much more easily along certain planes, their *planes of cleavage.*

Again, heat and electricity are conducted with perfect uniformity through amorphous bodies, while crystals conduct these impulses in specific directions.

Light passes through transparent crystals with varying velocity in different directions; through amorphous bodies with the same velocity in all directions.

Crystallisation is the forming of crystals from a solid body. The principal methods are as follows:

1. Hot water is poured over an excess of the solid, forming a hot saturated solution. This is filtered while hot and then allowed to cool.

2. The solid is dissolved in an excess of water and filtered. A diluted solution is obtained, and this is evaporated on a waterbath until a scum forms on the surface, indicating a hot saturated solution. This is then cooled.

3. A clear, diluted solution is allowed to stand until the solvent evaporates, leaving the solid in crystals.

4. The dry solid is melted and on being carefully cooled, form crystals. This is used to crystallise Sulphur

The most convenient manner of crystallising by fusion and partial cooling, is to melt the solid in a deep crucible, and cool it until a solid crust is formed on the surface. A hole is then

made through this, and as much as possible of the molten substance is poured out. Much adheres to the crust and to the sides of the crucible, and, when cool, this crystallises.

5. Sublimation is often used for crystallisation, especially for substances like Iodine.

The first three methods are based upon the separation of crystals from solution, and are most important.

A mother liquor is the liquid from which crystals have been obtained; it is still a saturated solution, and will yield more crystals on evaporation.

The largest and most perfect crystals are obtained when the cooling is effected very slowly and without agitation. If a hot saturated solution is rapidly cooled and at the same time shaken, the resulting crystals are very small. These are called *granulated salts* or *crystalline powders.*

Crystals form best on rough surfaces, as these offer many points for adhesion. For this reason, threads are often suspended in the solution. Wood and Lead strips are also used.

When portions of the smooth surface of a vessel are rubbed with a glass rod and somewhat roughened, the crystals form first on these places.

'Nursing' is the method of inducing large crystals by introducing small ones into a solution saturated with the solid of which they are composed. As the substance crystallises out, it will uniformly cover the small crystals, and each of these forms a nucleus for a much larger one.

Crystallisation is used as a means of purification. As a rule crystals are free from the other substances present in their mother liquor. Most crystalline substances have each their own peculiar crystal form, and this serves frequently as a means of identification.

Frequently crystals contain water chemically united to them and this is then said to be their *water of crystallisation.* This can be proven by heating them in a retort connected with a receiver. The crystals melt and a liquid distils into the receiver which is found to be pure water; while the salt remains

in an amorphous state in the retort. This suggests that the crystal form is dependent upon the water chemically bound in the crystals.

Two-thirds of the weight of some salts is water of crystallisation. Alum, Glauber's salt, Epsom salt, Zinc-sulphate, borax, copperas, and blue vitrol, all contain a considerable quantity.

Common salt, Potassium-bromide, Potassium-iodide, Potassium-chlorate, Silver-nitrate and some other salts do not contain any.

The laws of the constant and multiple proportions are applicable to the water of crystallisation. It is symbolised in formulae by placing the amount of water immediately behind the formula of the molecule, as

$$MgSO_4, 7\ H_2O$$

Exsiccation is the driving out of the water of crystallisation by heat. The salt remaining is said to be *burnt, exsiccated* or is called an *anhydrous salt.* Plaster of Paris (exsiccated Calcium-sulphate) and burnt alum (exsiccated Aluminum-Potassium-sulphate) are anhydrous salts.

Some crystals lose their water of crystallisation by exposure, and become fine powders—as Sodium-carbonate. They are said to be *efflorescent.*

If water is added to an exsiccated salt, it takes it up and resume the crystalline form. This explains why plaster of Paris solidifies when mixed with water.

Many salts having water of crystallisation form what is called an *aqueous flux* when heated. This is caused by the splitting of the crystal into the anhydrous salt and water, which causes the liquid condition. If the exsiccated salt is further heated, it will melt as all solids do when their temperature is sufficiently raised. This is known as the *fire flux.*

Some salts contain water *mechanically* enclosed within their interior, left there during crystallisation. This is the *water of decrepitation,* and causes the crystals to burst into fragments and fall apart when heated—the water being converted into vapor, the expansion of which causes this phenomenon. Common table salt is a familiar example. It is evident that this is

entirely different from the true water of crystallisation; the latter is chemically united with the salt, while the former is mechanically enclosed.

Each substance usually has one characteristic form only—it is *mono-morphous*. Sometimes, however, the conditions of crystallisation have an influence upon the shape and there are substances which can thus be obtained in two crystalline forms—they are *dimorphous*: or in many different forms—*polymorphous*.

In some instances different chemicals have the same crystal form; Potassium-bromide and Potassium-iodide both crystallise in cubes which are morphologically identical. These are *iso-morphous bodies* that is, they are chemically different, but have like crystal form. Epsom salts and Zinc-sulphate are isomorphous.

Isomorphous substances in the same solution always crystallise together and form *mixed crystals*. It is therefore impossible to separate isomorphous bodies by crystallisaton, as can be done where this is not the case.

If a crystal is brought into a saturated solution containing a substance with which it is isomorphous, it continues to grow; layers of the second substance being uniformly deposited on the crystal.

A very important law relating to the constitution of isomorphous bodies was discovered by Mitscherlich. It reads: *Isomorphous substances have analagous chemical composition*, the symbol of one element being replaced by that of another, as follows:

$MgSO_4$, $7H_2O$	isomorphous	with	$ZnSO_4$, $7H_2O$
KBr	"	"	KI

CHAPTER VII.

DETERMINATION OF MOLECULAR MASS AND ATOMIC MASS; CALCULATION OF CHEMICAL FORMULAE FROM ANALYSIS.

DETERMINATION OF MOLECULAR MASS.

The methods for the determination of the molecular mass of bodies are *chemical* and *physical.*

CHEMICAL METHOD.

An exact qualitative and quantitative analysis of the substance the molecular mass of which is desired is made, and the result expressed in percent. To illustrate this, let us take the molecular mass of acetic acid. It yields on analysis

Carbon, 40 percent,
Oxygen, 53.33 percent,
Hydrogen, 6.67 percent.

Now the smallest possible molecular mass is calculated.

As the molecule of any Hydrogen compound contains at least one atom of Hydrogen, *the smallest possible molecular mass is the number of grams which contain one gram of Hydrogen.*

As 100 grams of acetic acid contain, according to the analysis, 6.67 grams of Hydrogen, the smallest possible molecular mass is

$$100 : 6.67 = 15.$$

The true molecular mass is either equal to the smallest pos-

sible molecular mass or a multiple thereof; depending on the actual number of Hydrogen atoms in the molecule. Hence the true molecular mass of acetic acid must be 15 or a multiple thereof by the number of Hydrogen atoms in the molecule. This number is often determined by substituting another element for Hydrogen in the molecule.

In the case of an acid, a certain quantity of it is treated with a metal, and this causes all or part of the Hydrogen to be replaced and a salt to be formed. This salt is analysed in order to find out how much Hydrogen is still contained. If 15 grams of acetic acid, which contain 1 gram of Hydrogen, are treated with Sodium, Sodium-acetate is formed. The analysis of this shows it to still contain ¾gram of Hydrogen; hence, only ¼ gram of Hydrogen has been substituted by Sodium. As only *whole atoms* of Hydrogen can have been substituted (atoms being the limit of divisibility), it follows that the molecule of acetic acid must contain at least 4 atoms of Hydrogen, of which 1 is replaced by a metal when a salt is formed.

A great number of other investigations show that never less than a quarter of the Hydrogen in acetic acid is replaced by another element; and it follows that its molecule contains 4 atoms of Hydrogen and therefore its true molecular mass is four times that of the smallest possible molecular mass, or

$$15 \times 4 = 60.$$

PHYSICAL METHODS.

All physical methods are based upon the Avogadro's law. We have seen that the molecular mass of a gas or vapor is twice a great as its density (relative to Hydrogen).

1. *Gas or vapor density method.*

To obtain the molecular weight of gases and vapors (also of liquids and solids which are vaporisable) it is only necessary to determine their density, as gas, and multiply by two. If density is expressed in relation to air, this must be multiplied by 14.435, to obtain the density in relation to Hydrogen; for, as we have seen, air is 14.435 times as heavy as Hydrogen. This must be

then multiplied by two, as before, to find the molecular mass. Thus the density of the gas in relation to air, multiplied directly by 28.87, will also give the molecular mass. The number is called the *reduction coefficient* or *normal quotient.*

2. *By determining the depression of the freezing point.*

For the determination of the molecular mass of solids and liquids which cannot be evaporated, the method usually employed is the determination of the depression of the freezing point.

Raoults law states that the depression of the freezing point of a solvent brought about by dissolving a gram-molecule of any substance in 100 grams of it is the same in every instance for the same solvent. This law is applied as follows :

100 grams(g) of the solvent are placed in the tube of a Beckmann's apparatus and the freezing point noted. A certain weight (w) of the substance, the molecular mass of which is to be determined is dissolved in this, and the freezing point taken. The difference between the two freezing points is the freezing point depression (t).

Let the unknown molecular mass of the substance be symbolised by M and the freezing point depression produced by one gram-molecule in 100 grams of the solvent by D. Then one gram will depress the freezing point D:M and w grams would produce a depression of w.D : M. Then

$$t = \frac{w.D}{M}$$

or

$$M = \frac{w.D}{t}$$

If g grams are used in place of 100 grams of the solvent. the formula becomes

$$M = \frac{100.w.D}{t.g}$$

The fact that the molecular elevation of the boiling point of a definite solvent is the same for all dissolved substances offers another method.

DETERMINATION OF THE ATOMIC MASS.

1. *From the combining weight.*

It has been shown that the atomic mass of an element is equal to, or a simple multiple of, its combining weight. The combining weight can be determined by chemical analysis of the Hydrogen or Oxygen compounds as previously explained. It may also be determined by the substitution of *equivalents.* These are the weight-quantities of other elements which are able to replace one gram of Hydrogen in a Hydrogen compound. A third method is to pass an electric current through a series of different solutions of salts; the salts are decomposed, and the weight-quantities of the elements which are separated have the relation of their combining weights (*law of Farraday*).

2. *By determining the smallest mass of an element in any molecule.*

Atomic mass may also be defined as *the smallest mass of an element found in the molecule-mass of any of its compounds.*

In order to determine the atomic mass, a great number of compounds of this element with others are prepared. The molecular mass of each of these is determined according to the methods described, and quantitative analysis made in order to find out the number of grams of the element contained in one gram-molecule of each of its compounds. The smallest number found is then considered as the atomic mass.

3. *By the application of the Dulong-Petit law.*

Determination of the atomic mass can be made according to the Dulong-Petit law by dividing 6.4 by the specific heat. Although results obtained by this method are only approximate, yet, knowing the combining weight of the element (which can be determined exactly), it offers a method of accurately deciding the number by which to multiply the combining weight in order to get the atomic mass.

4. *By Isomorphism.*

Isomorphous substances are analagous in composition: the only difference between them being that one or more atoms in one of them are replaced by the same number of different atoms in the other. Consequently their formulae are analagous, as in the case of Potassium-perchlorate ($KClO_4$) and Potassium-permanganate ($KMnO_4$).

The knowledge of the formula and other chemical data concerning a compound permits of the determination of the atomic mass of an element contained in a compound isomorphous with it. Suppose it is desired to learn the atomic mass of Manganese by this method; then a compound of known formula which is isomorphous with a compound of Manganese must be found. Potassium-perchlorate will be observed to be isomorphous with Potassium-permanganate; and as the formula for Potassium-perchlorate is known to be $KClO_4$, that of Potassium-permanganate will be $KMnO_4$.

The formula shows that the gram-molecule of Potassium-permanganate contains one atom-gram (39 grams) of Potassium. An exact chemical analysis is made and it is found that 39 grams of Potassium are contained in 158 parts of Potassium-permanganate; the molecular mass is, therefore, 158.

Now the formula $KMnO_4$ shows the molecule contains only one atom of Manganese, consequently the parts of Mn in 158 of the Potassium-permanganate will represent the atomic mass of Manganese—it is 55.

CALCULATION OF CHEMICAL FORMULAE FROM ANALYSIS.

Chemical compounds are designated by *formulae*—water by H_2O, alcohol by C_2H_5OH, and so forth.

The formula invariably represents the molecule. H_2O means *one molecule* of water, C_2H_5OH *one molecule* of alcohol, etc.

The different atoms of elements which compose the molecule are shown in the formulae by *symbols,* these being capital letters. The letter which symbolises an element is the initial letter of its latin name. If the names of more than one element begin with the same letter, one is symbolised by the letter itself,

and the others by adding the next differential letter in the title, in this manner:

Carbon, C.	Chlorine, Cl.	Copper, Cu
Cadmium, Cd.	Chromium, Cr.	Calcium, Ca.
Caesium, Cs.	Cobalt, Co.	Cerium, Ce.

A symbol invariably means one atom of an element.

A numerical placed at the foot of a symbol indicates the number of atoms.

$$O_4 = 4 \text{ atoms of Oxygen.}$$

A portion of a formula written in parenthesis is a *radicle* (see later). SO_4 in the formula $Al_2\ (SO_4)_3$ is a radicle.

A figure placed after a parenthesis denotes the number of times the enclosed radicle is taken; SO_4 is taken three times in the above illustration. The formula might also be written $Al_2S_3O_{12}$, these figures being obtained by multiplying out.

A numerical *before* a chemical formula represents the number of *molecules*. $3H_2O$ denotes three molecules of water, each containing two atoms of Hydrogen and one of Oxygen; or six atoms of Hydrogen and three atoms of Oxygen in all.

To determine experimentally the chemical formula of a compound consisting of elements whose atomic mass is known, the following procedure is adopted:

(a). An exact quantitative and qualitative analysis is made.

(b). The molecular mass of the compound is determined by any of the methods given.

(c). The quantity of each element in the molecular mass is calculated from the percentage found on analysis.

(d). These quantities are divided by the atomic masses of the elements they represent, and the number of atoms of each element contained in the molecule is obtained

As an example, we may determine the formula of acetic acid.

(a). The quantitative analysis shows

Hydrogen, 6.667 percent;
Carbon, 40 percent;
Oxygen, 53.333 percent.

(b). The molecular mass is found to be 60.

(c). According to the analysis, the molecule mass (60 parts) contains

Carbon, 24.
Hydrogen, 4
Oxygen, 32.

(4). As 12, 1 and 16 respectively are the atomic masses of Carbon, Hydrogen and Oxygen, it is evident that the number of atoms of each element present is

$$C\ \frac{24}{12}\ H\ \frac{4}{1}\ O\ \frac{32}{16} = C_2H_4O_2.$$

CHAPTER VIII.

VALENCE: THEORY OF THE LINKING OF ATOMS.

When the chemical formulae of all known compounds are established in the manner described in the last chapter, a resemblance is noticed between many of them. This has led to their grouping according to their similarities.

The simplest chemical compounds are those consisting of but two elements; these are called *binary compounds.* A study of the binary compounds of Hydrogen shows that they can be arranged in four classes:

I.	II.	III.	IV.
HCl	H_2O	H_3N	H_4C
HBr	H_2S	H_3P	H_4Si
HI	H_2Se	H_3As	
HF	H_2Te	H_3Sb	

The first class consists of compounds containing one atom the second those containing two atoms, the third those with three atoms, and the fourth those having four atoms of Hydrogen combined with one atom of the second element. It is evident that the atom of each different element unites with its own peculiar number of Hydrogen atoms, and this number is the *chemical value, quantivalence or atomicity* of the element.

Therefore

The valence of Cl, Br, I and F is 1
The valence of O, S, Se and Te is 2
The valence of N, P, As and Sb is 3
The valence of C and Si is 4

The valence of an element may be established by preparing a binary Hydrogen compound of it, and then ascertaining how many atoms of Hydrogen are combined with one atom of the element. But Hydrogen compounds of few elements can be obtained and the valence of many elements can not be determined in this manner. Chlorine, however, often substitutes Hydrogen in the proportion of atom for atom; an atom of Chlorine, therefore, performs the same office as an atom of Hydrogen, and the compound formed is analagous to that with Hydrogen. This is illustrated in the formulae of the Chlorine substitution compounds:

PH_3	PCl_3
AsH_3	$AsCl_3$
CH_4	CCl_4
SiH_4	$SiCl_4$

Thus if the Hydrogen compound of an element is not known, the formula can be deduced from a Chlorine compound, if one of these is known. The formula of Zinc-chloride is $ZnCl_2$ and if a Hydrogen compound exists it will have the formula ZnH_2. The valence of Zinc is therefore 2.

The adaptation of this method renders the determination of valence much easier, as binary Chlorine compounds of most of the elements are known. But many elements form more than one compound with Chlorine. The chlorides of Tin will demonstrate this. There are two of them recognised, $SnCl_2$ and $SnCl_4$; showing that Tin has a valence of 2 and 4.

The determination of the valence from the formulae of the chlorides shows that elements may have several different valences. Also that

Elements exist with a valence of 5 and 6, as evidenced by the formulae PCl_5 and WCl_6.

Oxygen compounds are also used for the determination of valence. As oxides of all elements (except Fluorine) are known, and as these have been more thoroughly investigated than any other class of compounds, they may be used advantageously for this purpose.

When deducing the valence of an element from the formula of its oxide, it must be remembered that the valence of Oxygen itself is 2, and that *one* atom of Oxygen takes the place of *two* atoms of Hydrogen.

To deduce valence from an oxide, note the number of Oxygen atoms combined with one atom of the second element, and multiply this number by two.

The formula for the oxide of Aluminum is Al_2O_3. As two atoms of Aluminum have united with three atoms of Oxygen, one atom of Aluminum has united with 1½ atoms of Oxygen; and as each atom of Oxygen equals two of Hydrogen, the valence of Aluminum must be 3.

The oxides show that there are elements which have valences as high as 7 and 8, seen by the formulae Mn_2O_7 and OsO_4. No element is known with a valence higher than 8.

The elements are divided into eight classes according to their valence:

Mono-valent or *uni-valent elements* or *monades* are those with a valence of 1, as Hydrogen.

Di-valent or *bi-valent elements* or *diades* are those with a valence of 2, like Oxygen.

Tri-valent elements or *triades* are those with a valence of 3. Aluminum is tri-valent.

Tetra-valent elements or *tetrades* are those with a valence of 4. Carbon is tetra-valent.

Penta-valent elements or *Pentades* are those with a valence of 5, like Nitrogen.

Hexa-valent elements or hexades are those with a valence of 6, like Sulphur.

Hepta-valent elements or heptades are those with a valence of 7, as Manganese.

Octo-valent elements or Octades are those with a valence of 8, like Osmium.

The valence of the elements is given on page 6.

To give the student a thorough appreciation of valence, it may be graphically represented by small lines or hooks, equal in number to the valence, which radiate from the symbol, as follows

One atom of Hydrogen.

```
H—
```

One atom of Oxygen

```
—O—
```

One atom of Aluminum

```
  |
—Al—
```

One atom of Carbon

```
  |
—C—
  |
```

One atom of Nitrogen

```
  | |
—N—
  |
```

One atom of Sulphur

```
  | |
—S—
  | |
```

One atom of Manganese

```
  ||
=Mn—
  ||
```

One atom of Osmium

```
  |||
—Os—
  |||
```

When atoms of two different elements combine, valences (hooks) of one atom link with those of the other; a single hook on one side being only able to link with one on the other.

```
     H
     |
H—C—H =CH 4
     |
     H
```

```
O
||
C = CO2
||
O
```

The building up of chemical compounds from atoms can be compared to the formation of a watchchain by the union of the different links. This method, which shows the relative position of the atoms, illustrates the *theory of the linking* or *chaining of atoms* and is adopted by all chemists.

Saturated molecules are those in which all valences are satisfied.

Unsaturated molecules are those in which not all the valences are satisfied.

Many scientists think that the existence of unsaturated molecules is impossible. Yet some few formulae are difficult of explanation if we deny the possibility of unsaturated molecules.

In thousands of compounds, Carbon is found to be tetra-valent; still, a compound exists of the formula CO (Carbon-mon-oxide) which, if there are no unsaturated molecules, would show Carbon to have a valence of 2 in this isolated instance. The existence of a di-valent Carbon atom, however, seems no more probable than that there exist compounds that are not satisfied.

Some atoms, with a valence of two or more—like Carbon, Oxygen and Sulphur, are able to link with fellow atoms of the *same* element with one or several of their valences, forming chains.

—O— —O— —O— —O—

Carbon is especially prone to do this; and as each atom is tetra-valent, three different ways of uniting two Carbon atoms are posssible.

1. *By single bonds.*

```
 |   |
—C— —C—
 |   |
```

2. *By double bonds.*

```
—C═C—
 |  |
```

3. *By triple bonds.*

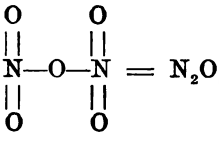
```
—C═C—
 |__|
```

CHAPTER IX.

CHEMICAL FORMULAE.

Graphical and Empirical Formulae:

The fundamental principle in developing chemical formulae is the linking together of atoms by their points of valence. We will assume that only saturated compounds are possible; that is, compounds wherein all the points of valence in the component atoms have linked into like points of valence of other atoms, so that none remain unsatisfied. The following formula illustrates this:



$$= N_2O_5.$$

Formulae like the above, which represent the valence of atoms by strokes, are called *structural, graphical* or *constitutional formulae;* while a formulae like N_2O_5, which does not explain the connection between the atoms, is an *empirical formulae.*

When there is any doubt as to the correctness of a formula, it must be established structurally; only a structural formula being regarded as conclusive.

Nomenclature of binary compounds.

A binary compound is one that contains only two elements and is designated by the ending *"ide."* A chlor*ide* is a compound of Chlorine and another element; an oxide is a compound

of Oxygen and one other element; etc. The second element in the compound is implied by the name; Zinc-oxide is a compound containing Zinc and Oxygen, Potassium-iodide a compound of Potassium and Iodine.

In binary compounds of metals with non-metals, 'ide' is added to the name of the non-metal; thus a compound of Zinc and Bromine is Zinc-bromide.

In the binary compounds of non-metals

The Oxygen compounds are *oxides.*

The Chlorine compounds (except those with Oxygen) are *chlorides.*

The Bromine compounds (except those with Oxygen) are *bromides.*

The Iodine compounds (except those with Oxygen) are *iodides.*

The compounds of Sulphur (except those with Oxygen, Chlorine, Fluorine, Bromine and Iodine) are *sulphides.*

In latin, the ending *"idum"* is used to signify a binary compound. The name of the element which carries the ending "idum" (ide in english), is prefixed by the name of the other element in the genitive form, as Zinci oxidum, Potassii bromidum, etc.

To construct graphical formulae

Write the symbol of one of the elements in the compound and let a number of lines equal to the valence of the element radiate from it. Then put down the symbol of the second element in the same manner, also representing the valence by lines. If we do this with Boron-oxide, we obtain:

Then unite the valence (hooks) of one element each with one of the other in such a manner that not more than one hook of the one element is linked with one hook of the other.

If the two elements have different valence, some of the hooks will remain unsatisfied, as follows:

$$—B{=}O$$

In this instance, one hook of Boron remains unsatisfied.

Now write down the symbol of another atom of the same kind as the atom whose valence is satisfied.

$$—O—\quad —B{=}O$$

and again join the valence of one with that of the other:

$$—O—B{=}O$$

If the valence of either remain yet unsatisfied, add another atom of the other element and join the hooks of valence:

$$={B}—O—B{=}O$$

Repeat this operation until all hooks of both elements are satisfied; taking care not to unite two atoms of the same element together. Then the structural formula for oxide of Boron will become

$$O{=}B—O—B{=}O = B_2O_3$$

of Zinc-bromide,

$$Br—Zn—Br = ZnBr_2.$$

of oxide of Columbium,

$$\begin{array}{ccccc} O & & O & & \\ || & & || & & \\ Cb & —O— & Cb & = & Cb_2O_5 \\ || & & || & & \\ O & & O & & \end{array}$$

Formulae developed in this way will always be correct.

To make empirical formulae.

(a). The preferable method is to develop the structural formula as above described, then to count the number of atoms of each element and write this down after the symbol to which it belongs, as was done in the above examples.

It is customary to write the symbol of the non-metal last in binary compounds of metals and non-metals; but in compounds of non-metals with non-metals the symbol of that element is generally written last which has the ending "ide."

(b). A second method is as follows:

1. Write the symbol of each of the two elements, and place over these the respective valence:

$$\overset{\text{III}}{\text{B}}\ \overset{\text{II}}{\text{O}}$$

2. Reverse the valence; that is, place the number which stands over one element at the foot of the other, thus:

$$\overset{\text{III}}{\text{B}}\ \overset{\text{II}}{\text{O}} = \text{B}_2\text{O}_3$$

3. Cancel if possible. This is not possible in this instance, so the formula is complete.

Develop the formula of Silicon-oxide.

1. $\overset{\text{IV}}{\text{Si}}\ \overset{\text{II}}{\text{O}}$
2. Si_2O_4
3. SiO_2

of Aluminum-oxide:

1. $\overset{\text{III}}{\text{Al}}\ \overset{\text{II}}{\text{O}}$
2. Al_2O_3
3. Cannot be cancelled.

To develop formulae where elements have varying valence. Here we have the followng rules:

1. If the element has two valences, the lower one is designated by the ending "*ous*;" the higher by the ending "*ic*." These are added to the latin name of the element.

Find the formula of Arsenous-oxide:

Arsenic has a valency of 3 and 5. The ending "ous" shows it to be tri-valent in this instance.

1. $\overset{III}{As}\ \overset{II}{O}$
2. As_2O_3
3. Cannot be cancelled.

Determine the formula for Antimonic-oxide:

Antimony has a valence of 3 and 5. The ending shows the element to be 5-valent in this compound:

1. $\overset{V}{Sb}\ \overset{II}{O}$
2. Sb_2O_5
3. Cannot be cancelled.

2. If the element has three or four different valences,

(a). The prefix *"hypo"* together with the ending *"ous"* signifies the lowest valence. In *hypo*chlor*ous* oxide, Chlorine is univalent.

(b). The ending *"ous"* without a prefix signifies the lowest valence but one. In Chlor*ous* oxide, Chlorine has a valence of 3.

(c). The ending *"ic"* without a prefix signifies the third valence from the lowest. In Chlor*ic*-oxide, Chlorine has a valence of 5.

(d). The prefix *"per"* together with the ending *"ic"* signifies the fourth valence from the lowest. In *per*chlor*ic*-oxide Chlorine has a valence of 7.

Find the formula of Sulphurous-oxide.

Sulphur has a valence of 2, 4 and 6; hence in this compound it

has the second lowest valence, 4.

	IV	II
1.	S	O
2.	S_2O_4	
3.	SO_2	

The formula for Permanganic-oxide will be:

Manganese has a valence of 2, 3, 6 and 7; the title signifies the fourth valence in this instance, and this is 7.

	VII	II
1.	Mn	O
2.	Mn_2O_7	
3.	Cannot be cancelled.	

Formula of Iodic-oxide:

Iodine has a valence of 1, 3, 5, and 7; the ending 'ic' signifies the third valence from the lowest, or 5.

	V	II
1.	I	O
2.	I_2O_5	
3.	Cannot be cancelled.	

Second method of naming binary compounds.

Beside the above method of nomenclature, in which the valence is denoted by the endings "ous" and "ic" and the prefixes "hypo" and "per," there is a second method—by adding to the word oxide, chloride, bromide, sulphide, etc., a prefix which implies the number of atoms of the element to which it is attached. These prefixes are:

Mon	1
Di	2
Tri	3
Tetra	4
Pent	5
Hexa	6
Hept	7

Thus pent-oxide of Phosphorus contains five atoms of Oxygen; di-sulphide of Carbon contains two atoms of Sulphur, etc.

As the compounds of Oxygen are very important for the development of the formulae of compounds of three or more elements, it is deemed advisable to give here a short treatise on the oxide.

OXIDES.

An oxide is a compound of Oxygen with one other element. All elements, with the exception of Fluorine and the Argon class, combine with Oxygen. The elements can be divided into eight classes, according to the formulae of their oxides:

1. Those in which *one* atom of Oxygen combines with *two* atoms of another element; forming an oxide of the general formula R_2O (Sodium, Potassium, etc.).

2. Those in which *two* atoms of Oxygen combine with *two* of another element, showing a general formula of R_2O_2, or cancelled, RO (Magnesium, Calcium, etc.).

3. Those in which *three* atoms of Oxygen combine with *two* of the other element, showing the general formula R_2O_3 (Aluminum, Boron, etc.).

4. Those which contain *four* atoms of Oxygen and *two* of the other element, showing the general formula R_2O_4 or cancelled, RO_2 (Carbon, Silicon, etc.).

5. Those in which *five* atoms of Oxygen combine with *two* of the other element, showing the general formula R_2O_5 (Nitrogen, Phosphorus, Arsenic, etc.).

6. Those in which *six* atoms of Oxygen combine with *two* of the other element, showing a general formula of R_2O_6 or, cancelled, RO_3 (Sulphur, Chromium, etc.).

7. Those in which *seven* atoms of Oxygen combine with *two* of the other element, showing a general formula of R_2O_7 (Chlorine, Manganese, etc.).

8. Those in which *eight* atoms of Oxygen unite with *two* of the other element, showing a general formula of R_2O_8 or, cancelled, RO_4 (Ruthenium).

Nomenclature of oxides.

Most elements form more than one oxide. For instance, Manganese forms six, MnO, Mn_2O_3, Mn_3O_4, MnO_2, MnO_3 and Mn_2O_7.

In cases like this, the particular oxide is specified by

1. The greek prefix mono- (1), di- (2), etc.; or

2. The prefixes hypo- and per-, and the endings -ous and -ic as previously explained.

Oxides of the formula R_2O_3 are sometimes called *sesquioxides* (sesqui- means one and one-half). Mn_2O_3 is sesquioxide of Manganese, for there are one and a half atoms of Oxygen to one of Manganese . This name, however, is only used in exceptional cases. If an element forms two oxides, both of which contain three atoms of Oxygen, the titles sesquioxide and trioxide are used to distinguish between them; but if an element has only one oxide which contains three atoms of Oxygen, it is called a trioxide whether the atoms of Oxygen are in the ratio of one and a half to one atom of the other element or not.

HYDROXIDES OR HYDRATES.

Many oxides, when treated with water, combine chemically with it and form *hydrates* or *hydroxides*. If a little water is added to lime, which is oxide of Calcium, the lime begins to steam, suffers a rise in temperature and falls into a white powder known as slaked lime. Water, added to pent-oxide of Phosphorus, causes the powder to become very hot and a colorless liquid is formed having a sour taste and acid reaction. In some cases water does not combine with the oxide.

There are three classes of hydrates:

1. Those which have a sour taste and redden blue litmus paper; These are *acids*.

2. Those which have a sharp, soap-like taste and which turn red litmus paper blue when dissolved, as slaked lime does. These are *bases*.

When bases and acids are brought together, they unite chemically and form a *salt*. This ability to form a salt with a base is an important characteristic of an acid, far more important than the sour taste and the effect on litmus paper. Not all acids taste sour, nor do they all turn blue litmus paper red, as we shall see later; all, however, combine with bases and form salts.

The most important property of a base is also its ability to combine with an acid and form a salt. Many bases are without the characteristic taste, and do not turn red litmus paper blue; but ,without exception, they combine with acids to form salts.

3. Those which have neither basic or acid properties, and do not combine with acids or bases.

These are *indifferent hydroxides.*

If an oxide combines with water, directly or indirectly, and forms an acid, it is said to be an *acid-forming oxide* or *acid anhydride.*

If an oxide combines with water, directly or indirectly, and forms a base, it is a *base-forming oxide.*

If an oxide does not form an acid or a base when combined with water, it is an *indifferent oxide.*

THE ACIDS.

An acid is a substance which can combine with a base and form a salt. Acids, when soluble in water, generally have a sour taste and redden blue litmus paper—this latter is said to be an *acid reaction.*

Many acids are formed by the addition of water to the corresponding oxide:

$$SO_3 + H_2O = H_2SO_4$$

Sulphuric-oxide and water form Sulphuric acid

$$N_2O_5 + H_2O = H_2N_2O_6 = 2HNO_3$$

Nitric-oxide and water form Nitric acid.

$$P_2O_5 + 3H_2O = P_2H_6O_8 \text{ or } 2H_3PO_4$$

Phoshoric oxide and 3 mol. water form Phosphoric acid.

Acids like the above are called *oxy-acids.*

When an oxide combines with water, each atom of Oxygen in the oxide can combine with one molecule of the water to form two OH groups:

$$O + H_2O = 2OH$$

RADICLES—HYDROXYL.

The group OH is the *hydroxyl* or *water radicle.* It may be considered as water (H_2O) from which one atom of Hydrogen is removed. Groups like OH are *compound radicles.* They do not occur in a free state, but are met with in compounds where they act like a single element.

Many radicles are formed, theoretically, by removing Hydrogen atoms from a compound. They have a valence equal to the number of Hydrogen atoms removed. For instance, three compound radicles can be formed from CH_4, a well-known compound of Carbon and Hydrogen:

CH_4 Methane (marsh gas).

CH_3 A compound radicle; of above; valence, 1.

CH_2 A compound radicle of CH_4; valence, 2.

CH A compound radicle of CH_4; valence, 3.

CH_3, CH_2 and CH do not exist in the free state, but may be recognised in compounds, where the whole radicle acts like an element. If all four atoms are removed from CH_4, we obtain C; that is, an atom of the element Carbon—a 4-valent radicle.

Thus the atoms of elements appear to be radicles, and are named *simple radicles;* while radicles like OH, CH_3, CH_2 and CH are *compound radicles.*

HYDROXYL ACIDS.

We have seen that when an acid is formed by the addition of water to an oxide, an atom of Oxygen of the oxide combines with a molecule of water and forms two hydroxyl groups, which now take the place of the Oxygen atom in the oxide. This is shown in the following equation:

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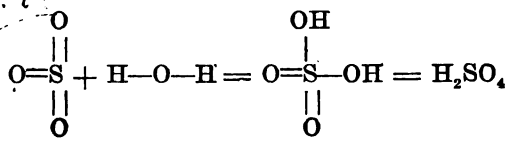
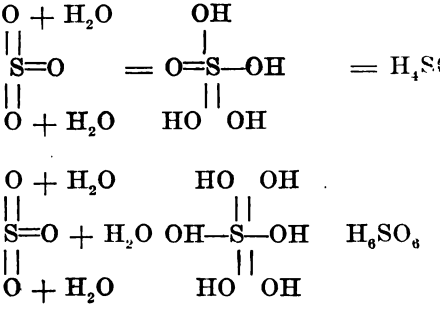


If an oxide has more than one atom of Oxygen (like SO_3), it is possible to gradually replace all by hydroxyl groups, two for each Oxygen atom:



There are, then, three different Sulphuric acids having the formulae H_2SO_4, H_4SO_5, and H_6SO_6.

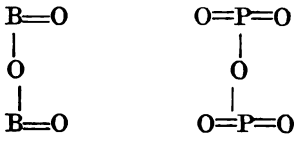
If all the Oxygen atoms in an oxide are replaced by hydroxyl groups, as in the last example $S(OH)_6$, the acid formed is a *perhydroxyl acid;* the others are named according to the number of hydroxyl groups they contain, as

$$H_2SO_4 \text{ or } SO_2(OH)_2 = \text{di-hydroxyl Sulphuric acid;}$$

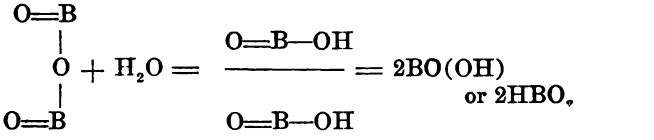
$$H_4SO_5 \text{ or } SO(OH)_4 = \text{tetra-hydroxyl sulphuric acid}$$

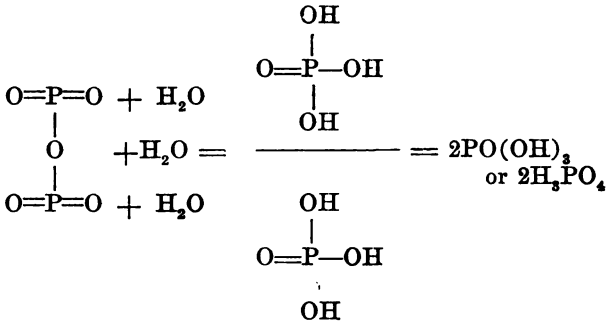
According to the foregoing, an acid oxide can form as many different acids as it contains oxygen atoms; each of these in turn being replaced by hydroxyl radicles.

In some oxides an atom of Oxygen links with two atoms of the second element:

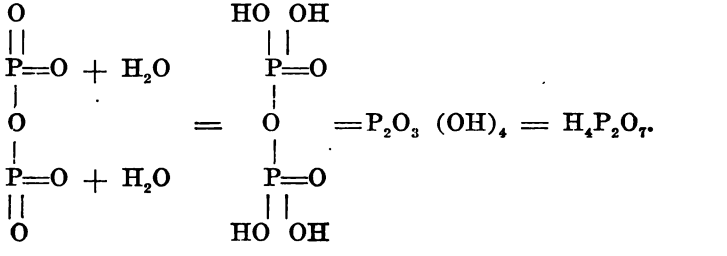


The central Oxygen atom connects the two Boron atoms or the two Phosphorus atoms as the case may be. If an oxide of this description combines with one molecule or with any odd number of molecules of water, the linking Oxygen atom is first replaced by the hydroxyl groups. The reason for this is that both have the same attraction for the water-molecule, and that Oxygen atom is therefore replaced which is equally distant from both. Hereby the connection between the two atoms is loosened; and, since univalent atoms or radicles are not able to link two other atoms together, the molecule of the oxide splits into two molecules of the acid.





But if such an oxide combine with an even number of water-molecules, the linking Oxygen atom is not the one replaced, but two Oxygen atoms which are each linked to one atom of the other element in the oxide, as follows:



Thus if an oxide in which two atoms of the second element are linked together by an Oxygen atom combines with an odd number of molecules of water, it splits and forms *two* molecules of acid; but if with an even number of molecules of water, it forms only *one* molecule of acid.

META, PARA (PYRO) AND ORTHO ACIDS.

As a general rule, those acids are of the most importance which are formed by the addition of one molecule of water to

the oxide; for instance, sulphuric, sulphurous, perchloric and carbonic acids are oxides, combined each with one molecule of water.

Acids formed by the addition of *one* molecule of water to the oxide are sometimes called *meta-acids;* as metaphosphoric acid, metaboric acid, etc. The acids of three- and five- valent elements like Phosphorus, Arsenic, etc., made by the addition of *two* molecules of water are *pyro-acids* (pyro-phosphoric, pyro-antimonic); while those acids of the same elements made by the addition of *three* molecules of water are the *ortho-acids* (ortho-phosphoric acid, ortho-boric acid). In acids of the four-valent elements (Carbon, Silicon, Tin), the prefix 'ortho' is used to indicate an acid with two molecules of water (ortho-carbonic acid, ortho-silicic acid, ortho-stannic acid).

To develop the formulae of acids.

According to the preceding, it is not difficult to construct the formula of any inorganic oxy-acid. It is necessary to

1. Write the formula of the oxide which the acid contains, according to the rules of the valence of the elements;

2. To add the molecules of water to this and

3. To cancel if possible.

Nitric acid is nitric-oxide and water

$$N_2O_5 + H_2O = H_2N_2O_6 \text{ or } 2HNO_3$$

Sulphuric acid is sulphuric-oxide and water

$$SO_3 + H_2O = H_2SO_4$$

If the prefix *meta-* is used, only one molecule of water is added to the oxide, as in the preceding examples. If the prefix *pyro-* is used, two molecules of water are added to the oxide. If the prefix *ortho-* is used, three molecules of water are added in the case of tri- and penta-valent elements, but only two in the case of tetra-valent elements. For instance

Pyrophosphoric acid is phosphoric-oxide and two molecules of water.

$$P_2O_5 + H_2O + H_2O = H_4P_2O_7$$

Ortho boric acid is boric-oxide and three molecules of water.

$$B_2O_3 + H_2O + H_2O + H_2O = H_6B_2O_6 \text{ or } 2H_3BO_3$$

Ortho-stannic acid is stannic-oxide and two molecules of water.

$$SnO_2 + H_2O + H_2O = H_4SnO_4$$

POLY- ACIDS.

Some of the acids are formed from more than one molecule of the oxide; and various amounts of water (1, 2, 3, 4, 5, etc. molecules) are added. Sulphuric-oxide yields an acid of the following formula:

$$SO_3 + SO_3 + H_2O = H_2S_2O_7$$

Silicon-oxide forms the following silicic acid:

$$SiO_2 + SiO_2 + H_2O + H_2O + H_2O = H_6Si_2O_7$$

The general formula of these acids is n molecules of the oxide + m molecules of water; n and m representing varying numbers. They are named *poly- acids.*

To illustrate how the atoms are connected in such acids, two, three and so on molecules of an oxide are theoretically combined as follows:

```
O=S=O
  ||
  O O      = S2O6 or 2SO3
  ||
O=S=O
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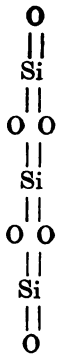
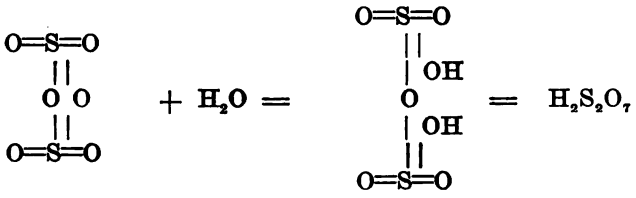


$= Si_3O_6$ or $3SiO_2$

We see from the first example that the theoretically possible multiples (polymeres) of the original oxide-formulae are obtained by connecting one Sulphur atom with its fellow by two bonds, each bond passing over an Oxygen atom, causing a two-fold indirect linking of the Sulphur atoms. This occurs in the case of Silicon and all other poly-acids.

By adding one molecule of water to an oxide of this description one atom of Oxygen is replaced by two hydroxyl groups:



The most important of these acids are fuming sulphuric acid ($H_2S_2O_7$), di-boric acid contained in borax, and those silicic acids which are contained in minerals.

If the poly- acid is made up from two molecules of the oxide, it is a *di- acid;* as di-chromic acid, di-sulphuric acid.

If made from three molecules, it is a *tri- acid,* etc.

ACID ANHYDRIDES.

As the acid-forming oxides may be considered as acids less water, they are sometimes called *acid anhydrides* (acid without

water). The anhydide can be obtained from an acid by subtracting all water from the formula of the acid, so that no Hydrogen remains:

$$H_2SO_4 - H_2O = SO_3$$

(Anhydride of sulphuric acid).

If an acid has an odd number of Hydrogen atoms, we must duplicate the formula before subtracting the molecules of water: In the case of Nitric acid, HNO_3, this would be

$$H_2N_2O_6 - H_2O = N_2O_5$$

Anhydride of Nitric acid.

MONOBASIC, DI-BASIC AND TRI-BASIC ACIDS.

As we will see later, the salts are formed by replacing the Hydrogen atoms of an acid by basic radicles. If an acid has only one atom of Hydrogen which can be replaced, it is called a *mono-basic* acid; if an acid has two atoms of Hydrogen which can be replaced in this manner, it is a *di-basic acid;* and if three atoms of Hydrogen can be replaced by basic radicles, it it is a *tri-basic acid,* and so on. Nitric acid is mono-basic, sulphuric acid is di-basic, and phosphoric acid is tri-basic.

ACID RADICLES AND ACID GROUPS.

There are two kinds of radicles obtained from acids:

1. *The -yl radicles of acids.*

A -yl radicle of an acid is the group which is left when the hydroxyl groups of the acid are removed. For instance, the -yl radicle of nitric acid (NO_2OH) is NO_2. Below are a few others:

SO_2= sulphuryl (sulphuric acid)
SO= thionyl (sulphurous acid)
NO_2— nitroxyl (nitric acid)
NO— nitrosyl (nitrous acid)
CO= carbonyl (carbonic acid).

Then the acid -yl radicles are the groups which combine with the hydroxyl groups to form the acid. The valence of this radicle is equal to the number of hydroxyl groups with which it combines in the acid. The valence of NO_2, the radicle contained in nitric acid, is 1, for it combines with one OH group to form nitric acid.

The radicle SO_2 has a valence of 2, as it combines with two OH groups in sulphuric acid.

Especially in organic chemistry do these radicles occur.

2. *The salt-forming radicles of the acids.*

When acids combine with metals and form salts, the Hydrogen atoms of the acid which are contained in the OH groups are the ones replaced by atoms of the metal. The groups which remain when the Hydrogen atoms are thus removed from the acids are the *salt-forming radicles.*

NO_3 is the radicle of nitric acid; SO_4 the radicle of sulphuric acid, etc.

The valence of such groups is equal to the number of Hydrogen atoms omitted; hence the nitric acid group NO_3 has a valence of 1, and the sulphuric acid group SO_4 has a valence of 2.

These groups are also real radicles, as they behave like a single element.

When speaking of acid radicles, we will imply those which are formed by removing the Hydrogen in this manner.

Radicles are generally written in parenthesis, and it is often convenient to write their valence over them in roman numericals as shown below:

$$\overset{\mathrm{I}}{(NO_3)} \qquad \overset{\mathrm{II}}{(SO_4)} \qquad \overset{\mathrm{III}}{(PO_4)} \qquad \overset{\mathrm{IV}}{(P_2O_7)}$$

HYDRO- ACIDS.

There is another class of acids, which differs widely from the oxy-acids just described. They do not contain any Oxygen and are binary compounds, one of the constituent elements being Hydrogen. Hydrochloric acid is a compound of Hydrogen and Chlorine; and as both are univalent, its formula is HCl.

Hydro-sulphuric acid is a binary compound of Sulphur and Hydrogen

$$\begin{array}{cc} \text{I} & \text{II} \\ \text{H} & \text{S} \end{array}$$
$$H_2S$$

Hydrobromic acid is a binary compound of Hydrogen and Bromine; and, as both are univalent, has the formula HBr.

SULPHO- OR THIO ACIDS.

Another class of acids is very similar in construction to the oxy-acids, but all, or part, of the Oxygen in them is replaced by Sulphur.

The common carbonic acid has the formula H_2CO_3, the sulpho-carbonic acid has the formula H_2CS_3.

To develop the formula of a sulpho-acid, that of the oxy-acid is made first, and then the Oxygen atoms are replaced by Sulphur atoms.

Ortho-sulph-antimonic acid would be

$$Sb_2O_5 + 3H_2O = H_6Sb_2O_8 \text{ or } 2H_3SbO_4$$

Replacing the Oxygen atoms by Sulphur, we obtain the desired formula (H_3SbS_4).

SELENO AND TELLURO ACIDS.

These classes of rare acids are built like the oxy-acids and the sulpho-acids, except that Selenium or Tellurium replace the Oxygen

Ortho (oxy-) arsenic acid	H_3AsO_4
Ortho-sulpho-arsenic acid	H_3AsS_4
Ortho-seleno-arsenic acid	H_3AsSe_4
Ortho-telluro-arsenic acid	H_3AsTe_4

The formulae of these acids may be developed in the same way as the sulpho acids.

Hydrogen in acids.

Hydrogen is in *all* acids, while the other constituent elements may vary. Hydrogen is, then, the acid-forming element.

BASES.

Bases combine with acids and form salts. A base, if soluble in water, has a sharp, soap-like taste and turns red litmus paper blue; this last is the *alkaline reaction.*

Many bases are formed from basic oxides by the addition of the elements of water:

$$CaO + H_2O = CaO_2H_2 \text{ or } Ca(OH)_2$$

$$K_2O + H_2O = K_2O_2H_2 \text{ or } 2KOH$$

Hence bases, like acids, are hydrates, compounds of oxides and water.

If we investigate which of the elements form bases and which acids, we find

1. The hydroxides of all elements which have a distinctly metallic character, are bases; as hydrates of Potassium, Calcium, etc.

2. Elements of a distinctly non-metallic character, like Chlorine, Sulphur and Phosphorus, form hydrates which are acids.

3. Elements which have no distinct metallic or non-metallic character form hydroxides which are both bases and acids, like Tin.

As metals form bases, they are also called the basic elements.

To develop the formulae of bases.

The formulae of bases are constructed in the same manner as the formulae of the acids, viz: by adding for each atom of Oxygen one molecule of water, the Oxygen atoms in the oxide being replaced by the hydroxyl groups:

$$CaO + H_2O = Ca(OH)_2$$

When two atoms of a metal in an oxide are linked together by an Oxygen atom, as in K_2O or Bi_2O_3, it splits into

two molecules of the base by the addition of an odd number of water molecules, just as is the case with the acids.

$$\begin{array}{c} K \\ | \\ O \\ | \\ K \end{array} + H_2O = \frac{KOH}{KOH} \text{ or } 2KOH$$

$$\begin{array}{l} Bi{=}O + H_2O \\ | \\ O \quad + H_2O \\ | \\ Bi{=}O + H_2O \end{array} = \frac{\begin{array}{c} HO\ OH \\ \| \\ Bi{-}OH \end{array}}{\begin{array}{c} Bi{-}OH \\ \| \\ HO\ OH \end{array}} = 2Bi(OH)_3$$

A metallic oxide can form as many hydrates as it has Oxygen atoms:

$$\begin{array}{l} Al{=}O \\ | \\ O \\ | \\ Al{=}O \end{array} + H_2O = \frac{\begin{array}{c} Al{=}O \\ | \\ OH \end{array}}{\begin{array}{c} OH \\ | \\ Al{=}O \end{array}} = 2\ AlO.OH \text{ (diaspor)}$$

$$\begin{array}{l} Al{=}O + H_2O \\ | \\ O \\ | \\ Al{=}O + H_2O \end{array} = \begin{array}{c} HO\ OH \\ \| \\ Al \\ | \\ O \\ | \\ Al \\ \| \\ HO\ OH \end{array} \quad Al_2O(OH)_4 \text{ (bauxite)}$$

$$\begin{array}{l} Al{=}O + H_2O \\ | \\ O \qquad + H_2O = \\ | \\ Al{=}O + H_2O \end{array} \qquad \begin{array}{c} OH \\ | \\ Al \\ \| \\ HO\ OH \\ \hline HO\ OH \\ \| \\ Al \\ | \\ OH \end{array} = 2Al(OH)_3 \text{ (hydrargillite)}$$

Three hydroxides from ferric-oxide (Fe_2O_3) are known, namely FeO.OH, goethite; $Fe_2O(OH)_4$, yellow iron ore; $Fe(OH)_3$, freshly-prepared ferric hydrate.

The bases which show the basic characteristics most markedly are those in which all Oxygen of the oxide is replaced by hydroxyl groups. $Al(OH)_3$ is a far stronger base than AlO.OH. The last has acid properties and may be called aluminic acid ($HAlO_2$).

Bismuth (Bi tri-valent) also forms bases in which all three Oxygen atoms are replaced by OH groups, and others where only one Oxygen atom is replaced.

$$\begin{array}{l} BiO + H_2O \\ | \\ O \qquad + H_2O = \\ | \\ BiO + H_2O \end{array} \qquad \begin{array}{c} OH \\ | \\ Bi{-}OH \\ | \\ OH \\ \hline OH \\ | \\ Bi{-}OH \\ | \\ OH \end{array} \quad 2\ Bi(OH)_3 \text{ Bismuth hydroxide.}$$

$$\begin{array}{l} Bi{=}O \\ | \\ O \\ | \\ Bi{=}O \end{array} + H_2O = \begin{array}{l} Bi{=}O \\ | \\ OH \\ \hline OH \\ | \\ Bi{=}O \end{array} \quad \begin{array}{l} 2\ BiO.OH \\ \text{Bismuthyl hydroxide} \end{array}$$

In Uranium-oxide (UrO_3) the most important base is not the one in which all three Oxygen atoms are replaced by the hydroxyl groups, $Ur(OH)_6$, but $UrO_2(OH)_2$; in which only one atom of Oxygen is replaced by hydroxyl groups. The best known Uranium salts are derived from this base and are called the Uran*yl* salts.

With the few exceptions named, we may say that the bases are formed from oxides, in which all of the Oxygen atoms are replaced by hydroxyl groups.

Development of the formulae of basic hydrates.

To construct quickly the formulae of true bases (those in which all O is replaced by OH groups), which are hydrates of metals, it is only necessary to add to the symbol of the metal a hydroxyl group for each point of valence; as

$$KOH \qquad Ca(OH)_2 \qquad Bi(OH)_3$$

RADICLES OF BASES.

The radicles of bases are theoretically formed by removing the hydroxyl groups. The radicle of $UrO_2(OH)_2$ is UrO_2, with a valence of 2—for two hydroxyl groups have been removed. The radicle of the base BiO(OH) is BiO, with a valence of 1. The majority of the formulae of true bases contain, beside the hydroxyl groups, only metallic atoms; and after removal of the hydroxyl groups only the metal itself remains. Hence the radicles of bases are metallic atoms, and only in rare instances are they groups (UrO_2, etc.).

When the radicle of a base is not a metal only but a compound radicle containing Oxygen, the name has the ending -yl. Uranyl, bismuthyl, antimonyl, are examples.

If a base has only one hydroxyl group, as KOH, it is a *mon-acid base;* if it has two hydroxyl groups, like $Ca(OH)_2$ it is a *di-acid base;* if it has three OH groups, it is a *tri-acid base,* and so on.

The varying character of the Oxides of metals.

Some metals (Manganese, Chromium, etc.), form several oxides, some of which are basic and others acid oxides. In such cases those of the oxides which contain the smaller quantity of Oxygen are basic oxides, while those which contain the larger quantity are acid oxides. Those which stand midway between the two are often indifferent. Thus Manganese forms

MnO or Mn_2O_2—basic oxide.

Mn_2O_3—basic oxide.

MnO_2 or Mn_2O_4—indifferent oxide.

MnO_3 or Mn_2O_6—acid oxide.

Mn_2O_7—acid oxide.

SULPHO- SELENO- AND TELLURO- BASES.

As we have sulpho-acids, seleno-acids and telluro-acids, we have also *sulpho-bases, seleno-bases* and *telluro-bases.* Their constitution is the same as that of the oxy-bases, except that they contain one of the elements named in place of Oxygen. For example:

KOH—Potassium hydrate.

KSH—Potassium sulph-hydratae.

KSeH—Potassium seleno-hydrate.

KTeH—Potassium-telluro-hydrate.

SALTS.

If an acid and a base are brought in contact, a chemical reaction takes place; they unite and form a salt and water:

$$KOH + HNO_3 = KNO_3 + H_2O$$

Base and acid form salt and water.

The acid properties of the acid and the basic properties of the base disappear, and the salt formed has entirely new properties. We cannot recognise by the senses that Epsom salt, Glauber's salt or blue vitrol contain sulphuric acid—which is, however, the case. If acid and base are mixed in proper proportions, the salt formed will have a *neutral reaction;* that is, it will change the color of neither red or blue litmus paper. The sour taste of the acid and the soap-like taste of the base also disappear, and the product of the reaction posesses a *salty taste.*

Not all acids are of acid reaction, not all bases turn red litmus paper to blue, nor do all salts have a neutral reaction and salty taste.

Only soluble salts have taste and action on litmus paper.

There are salts of neutral reaction which have a salty taste (Sodium-sulphate); others which have an acid reaction and sour taste(alum); some with an alkaline reaction and soap-like taste (Sodium-carbonate). Thus the reaction and the taste are not characteristic. The principal point of differentiation is that *salts are the product of the chemical union of acids and bases.*

Nomenclature of salts.

A salt contains two parts, a basic and an acid portion.

The metallic part of a salt is implied in the name; for instance Silver-nitrate contains the metal Silver; Copper-sulphate contains the metal Copper, etc.

The acid in a salt is indicated as follows:

1. If the name of a salt terminates in *-ate* (Sodium-sulphate, Potassium-nitrate), the name of the acid ends in -ic (in the above instances, sulphuric acid, nitric acid). The salts of sulphuric acid are thus seen to be sulphates, those of nitric acid nitrates, etc

2. If the name of the salt terminates in *ite* (Sodium-sulphite, Potassium-nitrite, etc.), the name of the acid from which it is derived terminates in -ous (sulphurous acid, nitrous acid, etc.). The salts of sulphurous acid are called sulphites, those of nitrous acid are called nitrites, and so on.

EXAMPLES.

Find the metal and the acid in Barium-permanganate.

The metal is barium, and the acid permanganic acid.

What metal and what acid are in Potassium-arsenite?

The metal is Potassium, and the acid arsenous acid.

First method of developing the formulae of salts.

(a). *Empirical formulae.* We may take as an example Calcium-orthophosphate.

The rules for writing the formula of a salt are as follows:

1. Put down the formula of the acid contained.

$$\text{Ortho-phosphoric acid} = H_3PO_4$$

2. Form the acid radicle by omitting the Hydrogen atoms and write this in parenthesis with the valence above (the valence being equal to the number of Hydrogen atoms replaced).

$$\overset{\text{III}}{(PO_4)}$$

3. Place the symbol of the metal, with the valence marked above, before the acid group.

$$\overset{\text{II}}{Ca}\ \overset{\text{III}}{(PO_4)}$$

4. Reverse the valence, and cancel if possible.

$$Ca_3(PO_4)_2$$

(b). *Structural formulae.*

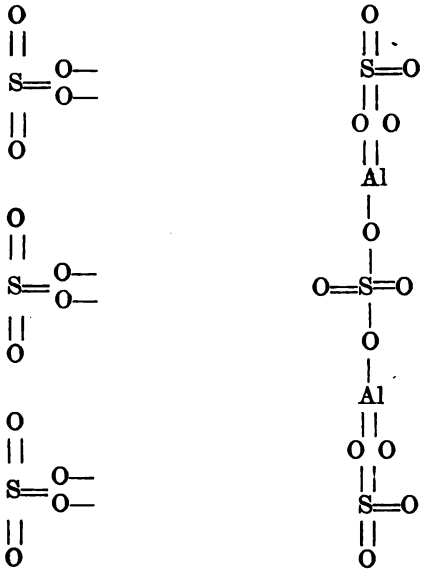
The structural formulae can be obtained from the empirical ones as follows:

Let us obtain the structural formula of $Al_2(SO_4)_3$ (Aluminum-sulphate) for example.

Write the structural formulae of the same number of

molecules of the acid as there are acid radicles in the empirical formula of the salt, omitting the Hydrogen atoms

2. Put the symbol of the metal down in the usual way and indicate the valence by lines; then connect the valence of the acid radicle with that of a metal, until all hooks are satisfied.



Second method of developing the formulae of salts.

First find the formula of the base—that is, the hydroxide of the metal; then the formula of the -yl radicle of the acid by removing the OH groups from the complete formula of the acid. Write over the acid -yl radicle its valence (the number of the OH groups removed). Now replace the Hydrogen atoms of the base by the -yl radicle of the acid, remembering that a univalent acid radicle replaces only one Hydrogen atom of the base, a di-valent two, and so on.

EXAMPLES.

Construct the formula of Bismuth-nitrate.

The base is Bismuth-hydroxide, $Bi(OH)_3$; the acid is nitric acid, $(NO_2.OH)$, the univalent radicle of which is NO_2. The formula of Bismuth-nitrate thus becomes

$$\begin{array}{l} O—NO_2 \\ | \\ Bi—O—NO_2 \\ | \\ O—NO_2 \end{array} = Bi(NO_3)_3$$

Sulphate of Calcium:

The base is Calcium-hydroxide,

$$HO—Ca—OH$$

and the acid sulphuric acid:

$$\begin{array}{c} OH \\ | \\ SO_2 \\ | \\ OH \end{array}$$

The -yl radicle, SO_2, is di-valent; as both radicles are di-valent, but one molecule of each is needed, and the formula becomes:

$$\begin{array}{c} O \\ || \\ Ca\ SO_2 \\ || \\ O \end{array} \text{ or } CaSO_4$$

Sulphate of Sodium.

The base is Sodium-hydroxide, NaOH; the acid is sulphuric, the radicle of which, SO_2, is di-valent. As the acid radicle has a valence of 2, two molecules of the base are needed; and as the basic radicle has a valence of 1, only one acid radicle is required. Then the formula of Sodium-sulphate becomes

3. The scientific method of naming an acid salt, is to indicate in the name the number of metallic atoms contained in it. This is done by using the prefixes mono-, di-, tri-, etc. as previously explained.

Mono-Sodium-carbonate = HO—CO—ONa.

This may also be called Sodium-bicarbonate, for half of the Hydrogen atoms are replaced.

Di-Sodium-carbonate = NaO—CO—ONa.

This is usually spoken of as Sodium-carbonate (normal).

Di-Sodium ortho-phosphate contains two atoms of Sodium.

Tri-Sodium ortho-phosphate contains three atoms of Sodium, etc.

4. Acid salts are sometimes named as follows:

(a). *Primary salts*—those in which one atom of Hydrogen is replaced by a metallic atom.

Primary ortho-phosphate of Calcium:

Orthophosphoric acid is H_3PO_4

$$\overset{II}{Ca}\ \overset{I}{(H_2PO_4)}$$

$$Ca(H_2PO_4)_2$$

(b). *Secondary salts*—those in which two atoms of Hydrogen are replaced by metallic atoms.

Secondary ortho-phosphate of Calcium:

Ortho-phosphoric acid is H_3PO_4

$$\overset{II}{Ca}\ \overset{II}{(HPO_4)}$$

$Ca_2(HPO_4)_2$ or, cancelled, $CaHPO_4$

(c). Tertiary salts—those which have three atoms replaced by metallic atoms.

Tertiary ortho-phosphate of Calcium:

Ortho-phosphoric acid is H_3PO_4

$$\overset{II}{Ca}.\overset{III}{(PO_4)}$$

$$Ca_3(PO_4)_2$$

In order to construct the formulae of an acid salt quickly, proceed as follows:

1. Write the formula of the acid.

2. Remove the necessary number of Hydrogen atoms from the acid formula and write the remaining acid group (including the remaining Hydrogen atoms) in parenthesis, with the number of the Hydrogen atoms removed placed above as valence. The number of Hydrogen atoms to be removed is indicated by the prefix.

For instance, in the case of bicarbonate of Calcium the acid group is

$$(\overset{\mathrm{I}}{HCO_3})$$

3. Write before the acid group the symbol of the metal, with its valence above.

$$\overset{\mathrm{II}}{Ca}\ (\overset{\mathrm{I}}{HCO_3})$$

4. Reverse the valence, and cancel if possible.

$$Ca(HCO_3)_2$$

Primary Calcium ortho-phosphate would be:

1. The acid is ortho-phosphoric acid, H_3PO_4.

2. Remove one Hydrogen atom, since the prefix primary is used.

$$(\overset{\mathrm{I}}{H_2PO_4})$$

3. Unite the metal and acid radicle by reversing the valence, cancel if possible.

$$Ca(H_2PO_4)_2, \text{ or } CaH_4(PO_4)_2$$

BASIC SALTS OR SUBSALTS.

Some normal salts, when treated with water and an excess of the base which they contain, combine with this excess and form *basic salts* or *subsalts*.

For instance, when normal Lead-acetate is treated with water

and oxide of Lead, sub-acetate of Lead is formed. This is a basic salt, since it contains an excess of the base. Only basic hydroxides with at least two Hydrogen atoms can form basic salts.

A great number of such salts are formed from bases (hydroxides of metals), by replacing part of the Hydrogen atoms of the base by acid -yl radicles. In sub-nitrate of Lead, the base is

$$HO—Pb—OH$$

and the acid contained is nitric acid, $NO_2.OH$; the -yl radicle of nitric acid is (NO_2) with a valence of 1, therefore sub-nitrate of Lead is

$$HO—Pb—ONO_2$$

The basic salts vary greatly in composition, and they may be considered as compounds of a certain number (n) of molecules of a normal salt with a certain number (m) of molecules of an hydroxide or oxide of the metal. Their general formula is therefore

n mol. of normal salt + m mol. of metallic oxide or hydroxide.

Sub-carbonate of Lead is $2Pb(CO_3) + Pb(OH)_2$

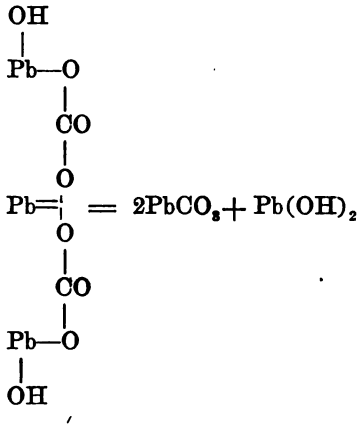
The connection of the atoms can be seen from the following:

The acid is carbonic acid,

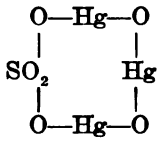
$$HO—CO—OH$$

the -yl radicle being CO with a valence of two. The base is hydroxide of Lead,

$$HO—Pb—OH$$



A basic salt which contains an oxide instead of a hydroxide, is sub-sulphate of Mercury, $HgSO_4 + 2HgO$. The atomic connection is as follows:



REACTION OF SALTS.

The reaction (neutral, acid or alkalinic) has no connection with the class to which a salt belongs. There are normal salts which have a neutral reaction (Sodium-sulphate), some with acid reaction (Zinc-sulphate), and still others with alkalinic reaction (Sodium-carbonate).

Even acid salts may have an alkalinic reaction (Sodium bi-carbonate).

DOUBLE SALTS.

In some instances, when two normal salts are brought together in solution and crystallised, the two unite chemically and form a *double salt*. There are two kinds of double salts:

1. Those in which the two component salts are derived from the same acid, but which have different bases. For example,

Sodium-Potassium-sulphate is a compound of
Sodium-sulphate and Potassium-sulphate.

Potassium-Aluminum-sulphate is a compound of
Potassium-sulphate and Aluminum-sulphate.

2. Those in which the component salts have the same base, but in which the acids are different; as

Schweinfurth green (Paris green) is a compound of
Copper-acetate and Copper-meta-arsenite.

The first class of double salts are formed by replacing the Hydrogen atoms of the acid (which must be at least di-valent), by two different metals.

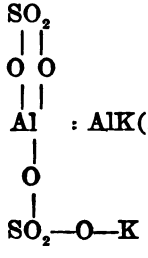
Sodium-Potassium-sulphate:

The acid is sulphuric acid, $HO—SO_2—OH$; then the salt is

$$KO—SO_2—ONa, \text{ or } KNaSO_4$$

Potassium-Aluminum-sulphate:

The acid is sulphuric acid, $HO—SO_2—OH$; the metals are Aluminum, with a valence of 3, and Potassium, with a valence of 1. An atom of Aluminum will need one and a half molecules of sulphuric acid to satisfy it, and the atom of Potassium half a molecule of the acid. Together they need two molecules of the acid. Thus the formula becomes



: $AlK(SO_4)_2$

The double salts of the second class are sometimes formed by

replacing the Hydrogen atoms of a base (which must be at least di-valent) by two different acid-radicals.

SULPHO SALTS.

Sulphur, as it is able to replace Oxygen in acids and in bases, is also able to do so in salts; these are *sulpho- salts.*

In order to develop the formula of a sulpho- salt, it is best to construct the formula of the oxy- salt, and then replace the Oxygen atoms in this formula by Sulphur atoms, thus:

Sodium-ortho-sulph-antimonate:

The formula of Sodium-orth-antimonate is Na_3SbO_4; replacing the Oxygen by Sulphur, we obtain

$$Na_3SbS_4 = \text{Sodium-ortho-sulph-antimonate}$$

SELENO AND TELLURO SALTS.

The formulae of these salts are made in the same way as the oxy- salts, substituting the Oxygen atoms by Selenium or Tellurium. They are of little importance.

PEROXIDES, PERSULPHIDES, ETC.

In addition to the binary compounds given before, we may mention the peroxides; these are binary Oxygen compounds containing more Oxygen than the ordinary oxide does. Peroxide of Hydrogen contains twice as much Oxygen as the regular oxide of Hydrogen (water). To explain the linking of the atoms in these compounds, we assume that one atom of Oxygen links by one of its valences with another atom of Oxygen, forming a chain of Oxygen atoms:

$$—O——O—$$

Then the free valence of the Oxygen atoms on each end are satisfied with other elements, thus:

$$H—O—O—H = H_2O_2, \text{ or Hydrogen-peroxide.}$$

$$\begin{array}{l} O—O \\ |\ \ | \\ Mn \end{array} = MnO_2, \text{ or Manganese peroxide.}$$

Isomers are chemical compounds having the same qualitative and quantitative composition, the same molecular mass, and belonging to the same general class; but which, nevertheless, exhibit different properties. The variation is caused by a different arrangement of the atoms in their molecules.

For instance, there are two substances of the formula C_4H_{10} (butane and iso-butane), both belonging to the same class but possessing different properties. An example of isomers in inorganic chemistry is the symmetrical and the asymmetrical sulphurous acid.

Metameres are chemical compounds which have the same quantitative and qualitative composition, the same molecular mass but belong to different classes. For instance, butyric acid and ethyl-acetate both have the empirical formula $C_4H_8O_2$; but the first is an acid and the second is not.

Polymers are chemical compounds which have the same qualitative and quantitative composition and belong to the same class of substances but differ in their molecular mass and therefore in their formulae: ethylene, C_2H_4, propylene, C_3H_6, and butylene, C_4H_8, are polymers.

Allotropy is polymerism of elements. A molecule of an element may contain different number of atoms. It causes the element to assume different properties. Ozone is a polymer of Oxygen.

CHAPTER X.

CHEMICAL EQUATIONS.

When a substance is chemically changed, it is said to undergo a *chemical reaction.* This may be brought about by heat, light, electricity, by the addition of another substance, etc., and is symbolised by a *chemical equation.* Upon the left side of the sign of equality are placed the *factors* entering into the reaction, connected by the plus sign (+); and upon the right side the product is written.

When a solution of Silver-nitrate is added to a solution of Sodium-chloride, a white precipitate of Silver-chloride and a solution of Sodium-nitrate are obtained.

FACTORS PRODUCT

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

Silver-nitrate and Sodium-chloride form
Silver chloride and Sodium-nitrate

These equations are also called *formulae equations,* or *reaction equations.*

Matter being indestructible, the sum of the weight-quantities of the factors of a chemical reaction must be equal to the sum of the weight of the product formed, or

the sum of the molecular masses on one side of an equation must equal the sum of those on the other. Thus

$$NaCl + AgNO_3 = NaNO_3 + AgCl.$$

		1 Ag	108	1 Na	23		
1 Na	23	1 N	14	1 N	14	1 Ag	108
1 Cl	35.5	3 O	48	3 O	48	1 Cl	35.5
mol. mass	58.5	mol. mass	170	mol. mass	85	mol. mass	143.5
	228.5				228.5		

Furthermore, as one element cannot be converted into another, it is evident that the quantities of each concerned in a chemical reaction will be the same before and after; or
the number of atoms of each element must be the same on both sides of the equation.

Whenever more than one molecule of a substance is treated of, it is indicated by prefixing a numerical to the formula.

In order to develop equations correctly, it is well to observe the following rules:

1. Determine the name of the factors acting on each other, and the name or names of the product.

The knowledge of what the products of the reaction are is essential to the development of the formula. As this knowledge constitutes a large part of Chemistry, is evidently impossible to give any one single rule which will enable the student to determine the product in all cases; these must be learned when studying the individual compounds. For the present we will supply the names of the factors and the product in order to show the steps necessary in the development of formulae.

We may take as an example the reaction of salt and sulphuric acid:

Sodium-chloride and sulphuric acid form
Sodium-sulphate and Hydrochloric acid.

2. Write the names of the factors engaged on the left side of the equation, and the name or names of the product on the right, connecting the different items on each side by the sign +.

Sodium-chloride + sulphuric acid =
Sodium-sulphate + Hydrochloric acid

3. Replace the names in the equation by chemical formulae, the development of which we have studied.

$$NaCl + H_2SO_4 = Na_2SO_4 + HCl.$$

4. Balance the equation; that is, equalise the number of atoms of each element on both sides.

If they are not equal when the respective formulae are written, it is necessary to place balancing numericals before those formulae containing less of any one element than is contained on the other side. In the above equation, the left side contains only one Sodium atom, and the right two. Therefore, the figure 2 is placed before NaCl,

$$2NaCl + H_2SO_4 = Na_2SO_4 + HCl.$$

The Sodium atoms on each side are equal.

Now count the atoms of the next element, Chlorine. There are two atoms on the left side (on account of the 2 placed before the NaCl, which indicates two *molecules* of NaCl, each with its atom of Chlorine), while on the right side there is but one. Thus it becomes necessary to place the figure 2 before HCl

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

If the atoms of Hydrogen, Sulphur and Oxygen be now counted, it is seen that the number of each is the same on both sides, viz:

2 Hydrogen, 1 Sulphur and 4 Oxygen.

Consequently, the above equation is correct.

Radicles like (SO_4) may be treated as indivisible groups and balanced in the same manner as a single element. It is advisable to check off the symbols of the elements, as balanced, by underlining.

The equation for the reaction between Sodium-carbonate, water and Aluminum-sulphate would be

1. Sodium-sulphate, Aluminum hydrate and Carbon-dioxide are formed.

2. Aluminum-sulphate + Sodium-carbonate + water = Sodium-sulphate + Aluminum-hydrate + Carbon-dioxide.

3. The formula for this is

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Na_2SO_4 + Al(OH)_3 + CO_2$$

4. But this is not a true equation as the number of atoms of each element on both sides are not equal. Therefore

(a). Balance the element Aluminum, and obtain

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Na_2SO_4 + 2Al(OH)_3 + CO_2$$

(b). Balance the radicle SO_4, which occurs three times on the left, but only once on the right;

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = 3Na_2SO_4 + 2Al(OH)_3 + CO_2$$

(c). Now balance Sodium, which has two atoms on the left and six (3 x 2) on the right;

$$AI_2(SO_4)_3 + 3Na_2CO_3 + H_2O = 3Na_2SO_4 + 2Al(OH)_3 + CO_2$$

(d). Balance Carbon, which has three atoms on the left, but only one on the right;

$$Al_2(SO_4)_3 + 3Na_2CO_3 + H_2O = 3Na_2\ (SO_4)_3 + 2Al(OH)_3 \quad + 3CO_2$$

(e). Balance Hydrogen, which has two atoms on the left, and six on the right;

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 3Na_2SO_4 + 2Al(OH)_3 + 3CO_2$$

(f). Balance the Oxygen (exclusive of the radicle SO_4, which is already accounted for). The $3Na_2CO_3$ on the left contains 9 atoms of Oxygen and the $3H_2O$ 3 atoms, or 12 atoms in all. The right side has 6 atoms in $2Al(OH)_3$ and 6 in $3CO_2$, also a total of 12 atoms. The Oxygen, then, is balanced.

The correct equation therefore reads

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 3Na_2SO_4 + 2Al(OH)_3 + 3CO_2$$

A thorough understanding of the working of equations is essential to a proper knowledge of chemistry. The following exercises should be worked out by the student:

Potassium-chlorate and Hydrochloric acid, when brought together, form Potassium-chloride, water and Chlorine; state this in the form of an equation.

Express by an equation the reaction which takes place when a solution of Potassium-carbonate and one of Calcium nitrate are brought together to form Calcium-carbonate and Potassium-nitrate.

Chemical equations, like mathematical ones, remain correct if both sides are multiplied or divided by the same number; or if from both sides the same number of like molecules are subtracted.

Two or more equations may be added together to form a single one; provided that the sum of all terms on the one side be shown to represent the sum of all the terms on the other. This fact is of great importance because a reaction often consists of several steps which immediately succeed each other. If diluted nitric acid acts upon Phosphorus, we may consider that three reactions take place:

1. The nitric acid is split up,

$$2HNO_3 = H_2O + 2NO + 3O$$

2. The Phosphorus unites with the Oxygen set free, forming Phosphorus-pentoxide

$$2P + 5O = P_2O_5$$

3. The Phosphorus-pentoxide unites with three molecules of water to form ortho-phosphoric acid

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

These equations may be added together, but it must be borne in mind that the amount of Oxygen set free in the first equation is not sufficient to oxidise the Phosphorus in the next step, because five Oxygen atoms are needed. In order to obtain just of each to form Phosphorus-pentoxide, it is necessary to take

$10HNO_3$ and 6P; this yields three molecules of P_2O_5. Therefore the steps in the reaction should read

$$1.\ 10\ HNO_3 = 5\ H_2O + 10\ NO + 15\ O$$
$$2.\ 6\ P + 15\ O = 3\ P_2O_5$$

Now, as equation 3 states the quantity of water which *one* molecule of Phosphorus-pentoxide takes up, it becomes necessary to multiply this equation by three, because there are three molecules of Phosphorus-pentoxide

$$3P_2O_5 + 9H_2O = 6H_3PO_4$$

The total of these three equations will be

$$\begin{array}{ll} 1.\ 10HNO_3 & = 5H_2O + 10NO + 15O \\ 2.\ 6P + 15O & = 3P_2O_5 \\ 3.\ 3P_2O_5 + 9H_2O & = 6H_3PO_4 \end{array}$$

$$10HNO_3 + 6P + 15O + 3P_2O_5 + 9H_2O = 5H_2O + 10NO + 15O + 3P_2O_5 + 6H_3PO_4$$

15O and $3P_2O_5$, which occur on both sides, may be cancelled; therefore

$$10HNO_3 + 6P + 9H_2O = 5H_2O + 10NO + 6H_3PO_4$$

As there are 9 H_2O on the left side and $5H_2O$ on the right, $5H_2O$ may be subtracted from each side

$$10HNO_5 + 6P + 4H_2O = 6H_3PO_4 + 10NO$$

This will cancel by 2:

$$5HNO_3 + 3P + 2H_2O = 3H_3PO_4 + 5NO$$

and this is the equation usually given to express this reaction.

If more than two equations are added, it is often advisible to add the first and second, and then the third to the total of the first two and so on.

In the reaction of nitric acid upon metallic Copper, three steps may be recognised:

1. A portion of the nitric acid splits up

$$2HNO_3 = H_2O + 2NO + 3O$$

2. The Copper is oxidised by the Oxygen set free

$$Cu + O = CuO$$

3. This is dissolved by another portion of nitric acid, forming Copper-nitrate and water

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$$

In combining these, 1 and 2 are first added together: as there are three atoms of Oxygen set free in equation 1, and but one utilised in equation 2, it is necessary to take enough Copper to satisfy all of the Oxygen, making equation 2 read

$$3Cu + 3O = 3CuO$$

The total of the two equations will therefore be

$$\begin{array}{r} 2HNO_3 = H_2O + 2NO + 3O \\ 3Cu + 3O = 3CuO \\ \hline 2HNO_3 + 3Cu = 3CuO + H_2O + 2NO \end{array}$$

3O being cancelled on both sides.

It is now necessary to add equation 3 to this:

But as there are three molecules of CuO, and only one was represented in the original equation, we must multiply by three. Then the total of the three equations will be

$$\begin{array}{r} 2HNO_3 + 3Cu = 3CuO + H_2O + 2NO \\ 3CuO + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2O \\ \hline 3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO \end{array}$$

3CuO being cancelled on both sides.

This final equation is the one usually given in text-books to express this reaction.

CHAPTER XI.

STOECHIOMETRY.

CALCULATION OF THE MOLECULAR MASS FROM THE FORMULA.

Stœchiometry is that branch of chemistry which relates to the calculation of chemical quantities; as the percentage composition of a body, the quantity of a chemical which can be prepared from a given amount of one of its compounds, etc.

Formulae, while serving the purpose of abbreviation, also represent molecular masses; that is, the sum of all the atomic masses contained. The formula of water (H_2O), beside showing a compound of Hydrogen and Oxygen, represents that the molecular mass of water is 18—this number being the sum of the atomic masses:

2 atomic masses of Hydrogen	2
1 atomic mass of Oxygen	16
	18

Hence the molecular mass of a compound can be calculated from the formula by adding the atomic masses contained.

It is advisable for the beginner to write down the atomic mass of the atom, multiply this by the number of atoms present, and add the results together—as shown above.

Carbolic acid (C_6H_6O) would then be

C_6 x 12	72
H_6 x 1	6
O_1 x 16	16
C_6H_6O	94

Find the molecular mass of $Al_2(SO_4)_3$.

The formula may also be written $Al_2S_3O_{12}$

Al_2 x 27	54
S_3 x 32	96
O_{12} x 16	192
$Al_2(SO_4)_3$	342

CALCULATION OF THE QUANTITY OF AN ELEMENT IN A COMPOUND AND QUANTITY OF A COMPOUND OBTAINABLE FROM A GIVEN QUANTITY OF AN ELEMENT.

This may be best illustrated by an example.

Let us determine the quantity of Oxygen in 108 grams of water.

1. Develop the formula of the compound.

This is found to be H_2O.

2. Calculate the molecular mass ofthe compound.

H_2 x 1	2
O_1 x 16	16
Water	18

3. Calculate the proportions of the masses of the different components.

Every 18 parts of water contain 2 parts of Hydrogen and 16 parts of Oxygen; or 2:18 is Hydrogen and 16:18 is Oxygen.

4. Apply this proportion to the total amount of the substance under consideration.

Of 108 grams water, 2:18 is Hydrogen and 16:18 Oxygen; therefore the amount of Oxygen contained is

$$\frac{16}{18} \times 108 = 96 \text{ grams.}$$

Determine in the above manner how much Lead-nitrate can be prepared from 410.7 grams of metallic Lead.

1. The formula is $Pb(NO_3)_2$.

2. The molecular mass is

P_1 x 205.35	205.35
N_2 x 14	28
O_6 x 16	96
$Pb(NO_3)_2$	329.35

3. The proportion of the masses of its components are

$$Pb\ \frac{205.38}{329.35} \qquad N\ \frac{28}{329.35} \qquad O\ \frac{96}{329.35}$$

It is evident that 205.35 parts is sufficient Lead for 329.35 parts of Lead-nitrate; therefore 410.70 grams will make

$$205.35 : 329.35 :: 410.70 : x$$

$$\frac{329.35 \times 410.7}{205.35} = 658.7 \text{ grams of Lead-nitrate.}$$

TO CALCULATE PERCENTAGE.

To calculate the percentage, figure the number of parts of the substance contained in a hundred parts.

Find the percentage of Silver in Silver-nitrate.

1. The formula is $AgNO_3$
2. The molecular mass is

Ag_1 x 108	108
N_1 x 14	14
O_3 x 16	48
$AgNO_3$	170

3. The proportions are

$$Ag\ \frac{108}{170} \qquad N\ \frac{14}{170} \qquad O\ \frac{48}{170}$$

4. Since there are 108 parts Ag in 170 parts $AgNO_3$, in 100 parts there will be

$$\frac{108 \times 100}{170} = 63.5 \text{ parts of Silver, or 63.5 percent.}$$

CALCULATION OF QUANTITIES ENTERING INTO CHEMICAL REACTIONS.

In cases where chemical compounds are brought together, it is necessary to illustrate the reaction by an equation, and to calculate from this the various quantities entering into, and obtained from the reaction.

EXAMPLE:

Silver-nitrate with Sodium-chloride forms Silver-chloride and Sodium-nitrate. How much Silver-chloride can be prepared from 340 grams of Silver-nitrate?

1. Make the equation.

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

2. Find the molecular masses and place them under the formulae, thus

$$\begin{array}{ccccccc} AgNO_3 & + & NaCl & = & AgCl & + & NaNO_3 \\ 170 & & 58.5 & & 143.5 & & 85 \end{array}$$

3. Calculate the proportions.

170 parts of $AgNO_3$ form 143 parts AgCl

4. Apply this proportion to amount under consideration.

If 170 grams of $AgNO_3$ form 143.5 AgCl, then 340 grams of $AgNO_3$ will form

$$170 : 143.5 :: 340 : x$$

$$\frac{143.5 \times 340}{170} = 287 \text{ grams Silver-chloride}$$

When a solution of Mercuric-chloride is mixed with a solution of Potassium-iodide, a red precipitate of Mercuric-iodide is produced, while Potassium-chloride goes into solution. Find the amount of Potassium-iodide needed for 813 grams of Mercuric-chloride.

1. Make the equation.

$$HgCl_2 + 2KI = HgI_2 + 2KCl$$

2. Determine the molecular masses.

$$\begin{array}{cccc} HgCl_2 + & 2KI = & HgI_2 + & 2KCl \\ 271 & 332 & 454 & 149 \end{array}$$

3. Calculate proportions.

271 parts of $HgCl_2$ need 332 parts of KI.

4. Apply this proportion.

If 271 parts of $HgCl_2$ need 332 parts of KI, then 813 grams of $HgCl_2$ will need

$$271 : 332 :: 813 : x \quad \text{or 996 grams of KI.}$$

CHAPTER XII.

SOME IMPORTANT CHEMICAL REACTIONS.

It now remains to explain at least a few of the more typical chemical reactions, and to give general rules by which to deduct the products formed. It will be evident that no one set of rules can be given which will cover the countless varieties of chemical processes. A few of the more common reactions follow.

Action of Acids on Basic Hydroxides.

If an acid acts upon a basic hydroxide, water and a salt of the acid with the metal are formed.

Nitric acid and Potassium-hydroxide form
Potassium-nitrate and water

Action of Acids on Basic Oxides.

If an acid acts on a basic oxide, water and the salt of the metal with the acid are formed.

Sulphuric acid and Zinc-oxide form
Zinc-sulphate and water

Action of Acids on Metals.

If an acid is able to dissolve a metal, a salt is formed. At the same time, secondary products are obtained. Metals are variously affected by different acids. Generally, the more easily a metal is oxidised, the more easily does it dissolve in an acid. Sodium and Potassium, which are so easily oxidised that they cannot be kept in air, are readily dissolved by acids; while Gold and Platinum, which have little affinity for Oxygen, are only

soluble in acids with difficulty. This fact is explained by the following law:

All metals must be oxidised and converted into basic oxides (or hydroxides) before they are able to dissolve in acids.

This law accounts for the secondary products formed when metals are dissolved in acids.

The Oxygen necessary for this may arise from three sources:

(a). It may come from the water present. Many metals, like Sodium and Potassium, take up Oxygen from water and evolve Hydrogen—other metals do the same in the presence of an acid; and this oxide then dissolves in the acid, forming a salt. If Zinc is treated with a dilute acid, two processes occur: first, the Zinc decomposes the water, forming Zinc-oxide and free Hydrogen:

$$Zn + H_2O = ZnO + H_2$$

and then the Zinc-oxide dissolves in the acid:

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

These two processes are usually expressed by the following misleading equation:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

This gives the impression that the Hydrogen generated comes directly form the acid, and that concentrated sulphuric acid and Zinc would likewise generate Hydrogen—which is not the case, as experimentation proves.

(b). The Oxygen may be derived from a part of the acid. This occurs in the case of acids like nitric acid, which readily give up part of their Oxygen; and in the case of metals having little affinity for Oxygen, and which do not decompose water. For instance, if Copper is dissolved in boiling sulphuric acid, the metal takes up one atom of Oxygen from the acid, forming Copper-oxide and sulphurous acid (H_2SO_3), which latter, when heated, splits up into Sulphur-dioxide and water:

$$Cu + H_2SO_4 = CuO + SO_2 + H_2O$$

Then the Copper-oxide dissolves in another molecule of sulphuric acid, forming Copper-sulphate and water:

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Adding the two equations and cancelling like formulae on both sides

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

As Copper and sulphuric acid have both the same valence, two molecules of sulphuric acid are necessary to dissolve one atom of Copper; one molecule of the acid being used to supply the Oxygen necessary for the oxidation of the Copper, the other to dissolve the Copper-oxide and form the sulphate.

(c). The Oxygen may be obtained from the air.

Copper, excluded form air, is entirely insoluble in dilute sulphuric or dilute hydrochloric acids, in vinegar or in fruit-acids. Even on boiling it remains insoluble, for the Copper cannot obtain the Oxygen necessary to form the oxide; it does not have affinity enough for Oxygen to take it from the water or from the diluted acid. If air be present, however, the Copper takes up Oxygen from this and forms the oxide, which then dissolves in the acid.

Action of Acids on Peroxides of Metals.

As a peroxide is an indifferent oxide and does not unite with acids or bases, it is necessary that it be changed into a basic oxide before it can unite with an acid. The basic oxide contains less Oxygen than the peroxide, therefore the latter must give up some Oxygen to form a basic oxide, which can then dissolve in the acid and form a salt.

If an acid acts on a peroxide of a metal, the salt, water, and free Oxygen are formed.

Sulphuric acid and Manganese-peroxide form
Manganese-sulphate, water, and Oxygen

The liberated Oxygen may induce secondary reactions:

(i) If the reaction takes place at low temperature, the liber-

ated Oxygen may unite in its nascent state with the water, forming Hydrogen-peroxide (H_2O_2).

Barium-peroxide and sulphuric acid form
Barium-sulphate and Hydrogen-peroxide

(ii) In the presence of hydrochloric acid, the Oxygen liberated oxidises some of this hydrochloric acid, forming water and free Chlorine.

In the presence of hydrobromic or hydroiodic acid, the liberated Oxygen acts upon them, frees the halogen element, and forms water.

Action of Acids on Acid Oxides or Other Acids

An acid has no chemical effect on another except in special cases. Chemical action of one acid upon another is seen when one of the reacting acids is a 'metallic' acid (metallic oxide plus water). Metals like Chromium and Manganese form several oxides; those richer in Oxygen being acid-forming oxides, those not so rich being basic-oxides. If a strong acid acts on such an acid-oxide or acid, the latter gives up Oxygen and forms the basic-oxide. This dissolves in the strong acid, forming water and a salt. If sulphuric acid acts upon Chromium-trioxide, the reaction occurs as follows:

$$2CrO_3 \text{ (acid-oxide)} = Cr_2O_3 \text{ (basic-oxide)} + 3O$$

$$Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O$$

Adding these equations, we obtain

$$2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + 3O$$

If a strong acid acts on an acid-oxide of a metal or on a metallic acid, a salt of the strong acid, water, and Oxygen are formed.

The liberated Oxygen can produce secondary reactions like those described above.

Action of Acids on Salts

(a). If the acid acting differs from the one in the salt.

(b). If the acid acting is the same as the one in the salt.

(*a*). *Action of Acids on Salts of Different Acids.*

An example of this kind is the action of sulphuric acid on Potassium-nitrate. There two different acids (nitric and sulphuric) and one metal (Potassium) are present.

The more powerful acid (that which possesses the stronger affinity) takes up the metal and forms a salt; while the weaker acid is set free.

In the instance given, sulphuric acid is more energetic than nitric acid, and takes the metal to form Potassium-sulphate—the weaker nitric acid being liberated.

The magnitude of chemical affinity depends primarily

(a) *Upon the relative quantities of the acting bodies.* The greater the quantity, the greater the energy.

(b). *Upon the solubility and volatility.* The less soluble or more volatile being correspondingly weaker.

The following table indicates the order of the relative affinities of a few acids at slightly elevated temperature:

Sulphuric acid.
Nitric and hydrochloric acids.
The majority of other acids.
Carbonic acid.
Hypochlorous acid.
Hydrocyanic acid.

This arrangement is subject to great variation, depending on temperature, relative quantities, degree of solution, etc.

(*b*). *Action of Acids on Salts of the Same Acid.*

I. If the salt is a normal salt.

(a). If the acid and metal are able to form an acid salt, this will be formed.

Sulphuric acid and Sodium-sulphate form
Sodium-bisulphate

(b). If the metal and the acid are unable to form acid salt, (in the case of mono-basic acids) no reaction occurs.

II. If the salt is a basic one.

If an acid acts on a basic salt of the same acid, the normal salt and water are formed.

Nitric acid and Bismuth-subnitrate form
Bismuth-nitrate and water

Action of Acid Oxides on Basic Oxides.

Water, and a salt of the acid and metal are formed.

Carbon-dioxide (acid-oxide) and Sodium-hydroxide
form Sodium-carbonate and water

Action of Acid Oxides on Basic Hydrates

The two oxides unite and form a salt.

Carbon-dioxide and Calcium-oxide
form Calcium-carbonate

Action of Basic Hydroxides on Basic Hydroxides

There is usually no reaction. There are some weaker basic hydroxides which, if treated with very powerful soluble basic hydroxides, act like acids and form salt-like compounds, liberating water. These may be considered as weaker hydroxides in which the Hydrogen atoms are replaced by atoms of the metal of the strong base:

$$HO—Zn—OH + 2KOH = 2H_2O + KO—Zn—OK$$

Action of Basic Hydroxides on Metals

There is usually no action, but there are some weaker metals like Zinc, Aluminum, etc., which, when acted upon by very powerful soluble metallic hydroxides, dissolve, evolve Hydrogen, and form a salt-like compound. In these compounds, the Hydrogen of the weaker base is replaced by the stronger metal:

$$Zn + 2NaOH = Na—O—Zn—O—Na + 2H$$

Action of Basic hydroxides on Normal Salts

This is an important reaction when the basic hydroxide is soluble in water, like those of Potassium, Sodium, Ammonium, Calcium, Barium and Strontium. If such a soluble hydroxide is added to a solution of a salt of a heavy metal, a precipitate is formed. This consists of the hydroxide of the heavy metal, the metal contained in the soluble hydroxide uniting with the acid radicle, and forming therewith a salt.

Ferric-sulphate and Potassium-hydroxide form
Ferric-hydroxide and Potassium-sulphate

Action of Basic Hydroxides on Acid Salts containing the Same Metal.

Water and the normal salt are formed.

Sodium-bisulphate and Sodium-hydroxide form
Sodium-sulphate and water

Action of Metals on Salts

The reaction depends on the magnitude of the affinity of the two metals for the acid. If the metal added has a greater affinity for the acid of the salt than the one originally contained, it will displace the weaker metal.

Copper-sulphate and Iron form
Iron-sulphate and Copper

The approximate affinity of a few of the more important metals for acids, commencing with the most energetic and ending with the least active, is given below:

Potassium, Sodium, Barium, Strontium, Calcium, Magnesium, Aluminum, Manganese, Zinc, Iron, Nickel, Cadmium, Lead, Tin, Bismuth, Copper, Silver, Mercury, Platinum, Gold.

The metals which are set free are often well crystallised, and form figures, *metallic trees* or *arbors*.

Action of two Entirely Different Salts on Each Other.

An insoluble compound is formed if possible.

Sodium-carbonate		Copper-carbonate
×	forms	and
Copper-sulphate		Sodium-sulphate

Each of the two salts brought together is soluble; but, on mixing, a precipitate of insoluble Copper-carbonate is formed.

It is suggested that the student indicate these reactions as follows:

Write the name of the salts one below the other

Sodium-sulphate
Calcium-chloride

Then make a cross, the lines of which unite the acid part of one salt with the basic part of the other

Calcium-chloride
×
Sodium-sulphate

Now consider if any of the salts implied by these connections are insoluble. In this example, Calcium-sulphate is insoluble and will precipitate.

Sometimes precipitates may be formed, though the cross indicates two soluble salts. If diluted solutions of Sodium-chloride and Ammonium-bicarbonate are mixed, no precipitation occurs. If concentrated solutions of these salts are mixed, however, Sodium-bicarbonate precipitates because it is less soluble than the factors, and not sufficient water is present for its solution.

CHAPTER XIII.

THERMAL EQUATIONS.

In chapter iv we have seen that heat facilitates chemical action within the limits of certain degrees of temperature; chemical action is also usually accompanied by the production or absorption of heat.

When Coal burns (unites with Oxygen), a great quantity of heat is freed, as we all know.

We distinguish between

Exothermic reactions—those chemical processes in which heat is produced; and

Endothermic reactions—those in which heat is absorbed (as in the union of Hydrogen and Iodine).

Isothermic processes are those in which no temperature change is recorded (melting of ice).

Thermo-chemistry investigates the relation between heat energy and chemical energy.

The chemical equations thus far studied

$$S + O_2 = SO_2$$

show only the qualitative and quantitative material changes caused by chemical action and do not express heat changes. Heat is liberated when Sulphur burns with Oxygen, equations like the above are therefore incomplete—the quantity of heat involved must be put down, as follows:

$$S + O_2 = SO_2 + 71.08 \text{ Calories.}$$

This means that when one atom-gram of Sulphur (32 grams) burns and unites with one gram-molecule (32 grams) of Oxygen, one gram-molecule (64 grams) of Sulphur-dioxide and 71.08 Calories of heat result.

Thermal equations express both the material change and energy change of chemical action.

Thermal value or *thermal modulus* is the quantity of heat involved (produced or absorbed) in a chemical reaction. For intance, in the above equation, the thermal value is 71.08 Calories. In this case heat was produced, and the process was therefore an exothermic reaction; while

$$H + I = HI - 1.5 \text{ Calories}$$

where heat is absorbed, is an endothermic reaction.

According to the principle of the conservation of energy, the heat liberated in exothermic reactions is not created, but merely passes from one state to another; in this instance, the source is the stored-up energy of the acting bodies.

The total quantity of energy of a mass is its *energy capacity or energy contents.*

The absolute amount of the energy contents of any body is unknown to us; but we may symbolise this unknown magnitude in the case of the atoms and molecules by writing the symbols in brackets,

(S) = unknown energy capacity of 1 atom-gram (32 grams) of Sulphur.

(O_2) = unknown energy capacity of 1 gram-molecule of Oxygen.

(SO_2) = unknown energy capacity of 1 gram-molecule of Sulphur-dioxide.

If we write the equation as follows,

$$(S) + (O_2) = (SO_2) + 71.08 \text{ Calories of heat}$$

we demonstrate that the energy of the products of an exothermic reaction must be less than the sum of the energy

capacities of the acting bodies; while the products of an endothermic reaction have a greater energy capacity than that of the sum of the acting bodies, as the following equation shows:

$$(H) + (I) = (HI) - 1.5 \text{ Calories.}$$

Thus we can measure the differences of the energy capacity of bodies by measuring the quantity of heat involved in a chemical action.

In writing thermal equations, the formula of the compound is sometimes omitted and the formulae of the acting bodies, separated by a comma, written in one bracket, as follows:

$$(S, O_2) = + 71.08 \text{ Calories}$$
$$(H, I) = -1.5 \text{ Calories}$$

Molecules which possess a great energy capacity will be especially liable to undergo chemical changes; that is, will be unstable. As endothermic processes lead to products which have a greater energy capacity than their factors, we conclude that products of endothermic reactions are unstable.

Hydroiodic acid, which is an endothermic product, is very unstable, splitting easily into Hydrogen and Iodine with the evolution of heat.

$$HI = H + I + 1.5 \text{ Calories.}$$

Hydrogen-dioxide, H_2O_2, is also an endothermic product and therefore splits easily into water and Oxygen:

$$H_2O_2 = H_2O + O + 23 \text{ Cal.}$$

Many products of endothermic reaction are explosive on account of their unstability. The formation of Nitrogen-chloride (NCl_3) can be expressed by the following endothermic equation:

$$N + 3Cl = NCl_3 - 41. \text{ Calories}$$

NCl_3 is extremely unstable, its decomposition into Nitrogen and Chlorine, which occurs even on the slightest contact of another body, being accompanied by a terrific explosion.

If endothermic compounds are unstable, it is logical to assume the compounds formed by exothermic reactions and possessing

a smaller energy capacity than the substances from which they are derived, will be stable; further to infer that the stability of compounds increases with the positive thermal value of the reaction by which they are formed. *The greater the quantity of heat which is disengaged in a chemical process, the greater the stability of the compound produced.*

We are further led to conclude that the tendency in chemical action is toward the formation of those products whose production is accompanied by the release of the greatest amount of heat.

The french chemist Berthelot realised this and called it *'le principe du travail maximum'* or the principle of the greatest work. In the main, chemical action really occurs according to this principle. Let us observe the reactions which take place when the hallogen elements (Fluorine, Chlorine, Bromine and Iodine) meet with Hydrogen. The thermal equations are:

$$H + F = HF + 37.6 \text{ Calories.}$$
$$H + Cl = HCl + 22 \text{ Calories.}$$
$$H + Br = HBr + 8.4 \text{ Calories.}$$
$$H + I = HI - 1.5 \text{ Calories.}$$

As the reaction of Fluorine on Hydrogen is accompanied by the greatest positive heat value, we conclude that the affinity of Fluorine for Hydrogen is the greatest; next, that of Chlorine, Bromine and Iodine respectively. We find this conclusion to be correct; for if Hydrogen is brought together with all four elements, it will first combine with Fluorine. When all Fluorine is satisfied, the Hydrogen will combine with Chlorine; next with Bromine and lastly with Iodine.

If Bromine is added to Hydroiodic acid, it unites with the Hydrogen and the Iodine is liberated:

$$HI + Br = HBr + I$$

9.9 Calories of heat are thus produced, the difference between the thermal values in the two equations of the reaction of Bromine on Hydrogen and that of Iodine on Hydrogen being 9.9 Calories (+ 8.4 and — 1.5).

Another instance of the ratio of the affinity of a body to the thermal value is seen in the case of Phosphorus. If red Phosphorus is made from the ordinary (yellow) form, the process is accompanied by the disengagement of heat, as follows:

$$P \text{ (yellow)} = P \text{ (red)} + 19.2 \text{ Calories.}$$

Hence the red Phosphorus possesess a smaller energy capacity than the ordinary Phosphorus; and if both unite with the same substance to form the same compound, the red variety disengages 19.2 Cal. less heat than the yellow because it contains so much less energy. The reaction with yellow Phosphorus will be more rapid.

That Berthelot's rule is not always correct is proven by the following example:

Sulphur forms, with Oxygen, SO_2 and SO_3; the thermal equivalents of these being

$$S + 2O = SO_2 + 71.08 \text{ Calories.}$$
$$S + 3O = SO_3 + 103.2 \text{ Calories.}$$

As in the latter case more heat is disengaged, we are led to expect that when Sulphur is burnt in air or Oxygen, this compound, SO_3, should be formed. But nearly all Sulphur, when burned, forms SO_2—although this is accompanied by the evolution of a lesser amount of heat.

Although Berthelot's principle does not possess the universal validity of a law, yet it holds good in so many instances that there is evidently something in it.

The thermal value of a chemical reaction is usually the sum of the values of several processes which take place simultaneously. Even such simple proceses as the union of two elements may be considered as consisting of three stages. When Chlorine unites with Hydrogen, forming Hydrochloric acid,

1. The Chlorine molecules which consist of two atoms, split into these atoms. As the decomposition of molecules into atoms is necessarily an endothermic process, because it is connected with an increase of volume, heat is absorbed. If we call this thermal value —a Calories, the equation becomes

$$Cl_2 = Cl + Cl - a \text{ Calories.}$$

2. The molecules of Hydrogen split up into atoms in the same manner, this also is an endothermic reaction. If we represent the thermal value in this case as —b Calories, the thermal equation may be written

$$H_2 = H + H - b \text{ Calories.}$$

3. One atom of Chlorine unites with one atom of Hydrogen, forming Hydrochloric acid. In this equation, which symbolises an exothermic reaction, heat is set free. If the thermal value of this equation is called + c, the equation becomes

$$H + Cl = HCl + c \text{ Calories.}$$

As there are, according to equations 1 and 2, two atoms of Chlorine and two atoms of Hydrogen which form two molecules of Hydrochloric acid, 2c Calories will be set free. Hence the heat quantity freed when one molecule of Hydrogen combines with one molecule of Chlorine is composed of three factors:

$$-a, -b \text{ and } + 2c$$

Then the thermal equation may be written

$$(Cl_2) + (H_2) = 2(HCl) + 2c - a - b$$

The combination of one atom-gram of each of Chlorine and Hydrogen produces 22 Calories; then the combination of one gram-molecule of each of these elements will produce 44 Calories and we obtain

$$(H_2) + Cl_2 = 2(HCl) + 44 \text{ Calories; or}$$
$$2c - (a + b) = 44 \text{ Calories.}$$

Thus the value +44 Calories comes from three sources. It is further evident that the sign of the thermal value (+ or —) depends upon the relative magnitude of 2c and (a + b).

We cannot consider the thermal value as a true measure of affinity, because this affinity is not the only factor in the thermal value.

Law of the constant heat consummation or *law of the equivalence of heat and chemical change.* Suppose we have a system consisting in its initial state of ammonia, NH_3, hydrochloric acid, HCl and water. We can produce the same change in this system in two different ways:

1. By uniting NH_3 with HCl to form NH_4Cl; and then dissolving this in water.

2. By dissolving the NH_3 and the HCl separately, each in half the amount of water; and then mixing the solutions thus obtained.

In both instances we start from the same initial state (A), NH_3, HCl and water, and reach the same final stage (B), an aqueous solution of ammonium-chloride . It is evident that in each of the single stages of these varying methods different quantities of heat are disengaged and absorbed; but as it is also true that the system has always the same energy capacity in condition A, and always the same energy capacity in condition B, it follows that

The sum of all energy quantities concerned in the change of a system from the same initial to the same final state is always the same and is not dependent upon the method by which the change is brought about.

CHAPTER XIV.

CHEMICAL EQUILIBRIUM.

If Sodium-chloride and Silver-nitrate act on each other, Sodium-nitrate and Silver-chloride are formed until all Sodium-chloride or all Silver-chloride, or all of both has completely changed according to the equation:

$$\underset{58.5}{NaCl} + \underset{170}{AgNO_3} = \underset{14.35}{AgCl} + \underset{85}{NaNO_3}$$

If the weight-quantities of the Sodium-chloride and the Silver-nitrate used are in the exact proportion of 58.5 : 170, both of these substances will be entirely converted and not a trace of Silver-nitrate or Sodium-chloride will be left; but if the proportion of the two reacting substances is different, the whole amount of that agent which is present in smaller quantity than the proportion requires is converted, while some of the reacting substance which is present in larger amount than necessary, remains unchanged after the reaction.

If a large quantity of Sodium-chloride acts upon a small quantity of Silver-nitrate, all Silver-nitrate is converted into Silver-chloride; while the excess of Sodium-chloride remains. Reactions of this kind, in which at least one of the reacting bodies is completely converted, are called *complete reactions.*

It is common belief with the beginner that all chemical reactions are complete and continue till at least one of the factors engaged is completely converted. Such complete reactions are, however, extremely rare—in fact, we may say that no chemical reaction is absolutely complete. Most reactions proceed to a limit where certain quantities of the reacting bodies are mixed together with certain quantities of the reaction products. An example will explain this:

If acetic acid ($CH_3.COOH$) acts upon alcohol (C_2H_5OH), ethyl-acetate ($CH_3COO.C_2H_5$) and water are formed,

$$\underset{60}{CH_3COOH} + \underset{46}{C_2H_5OH} = \underset{88}{CH_3COO.C_2H_5} + \underset{18}{H_2O}$$

If we mix 60 parts of acetic acid with 46 parts of alcohol, we should expect that all acetic acid and all alcohol will be converted into ethyl-acetate and water; but this is not the case. The reaction, as found by experiment, proceeds only until two-thirds of the acetic acid (40 parts) and two-thirds of the alcohol (30.667 parts) are converted; the liquid contains, in addition to the reaction products, some unconverted acetic acid and alcohol. The reaction is therefore incomplete.

When the factors of the equation are mixed in proper proportion, the experimental proof of partial decomposition can be given in many ways. Some very striking phenomena of coloration can be produced by these reactions: Ferric-chloride and Potassium-sulphocyanide, when brought together in solution, develop a blood-red color by the formation of Ferric-sulphocyanide. The maximum intensity of coloration would naturally be expected to occur when the factors are mixed in the proportion indicated by the equation; but we find that the coloration is intensified by the addition of an excess of Potassium-sulphocyanide. This shows that not all Iron is converted to red Ferric-sulphocyanide when mixed in proper propertion.

Theoretically, all chemical reactions are incomplete; but *practically* many reactions may be considered as complete, because the quantities of the reacting bodies which do not undergo change are so small that our present methods of analysing fail to detect them.

For instance if Hydrochloric acid is neutralised with Sodium-hydrate according to the equation

$$HCl + NaOH = NaCl + H_2O$$

we may consider the reaction as practically complete. Nevertheless, there are a number of good reasons for assuming that some of the Hydrochloric acid and of the Sodium-hydrate escape conversion, and that the product contains not only water and

Sodium-chloride, but also small quantities of Hydrochloric acid and Sodium-hydrate.

Chemical equilibrium is that condition of a chemical system in which the mutual reaction of the factors is at a standstill.

We have seen that when acetic acid and alcohol are mixed in molecular proportions, water and ethyl-acetate are formed until two-thirds of the acetic acid are converted, and the system here comes to a standstill. If now the two pure reaction products, water and ethyl-acetate, are mixed, a chemical reaction occurs in the opposite direction and alcohol and acetic acid are formed:

$$CH_3COO.C_2H_5 + H_2O = CH_3COOH + C_2H_5OH$$

We thus arrive at the remarkable fact that if pure reaction products are mixed in proper proportions and permitted to react upon each other under favorable conditions, they will decompose and again form the original factors. Therefore, the reaction sometimes occurs in the one direction, sometimes in the other.

Reactions of this kind are *reversible* or *reciprocal reactions.*

Acetic acid and alcohol $\rightleftharpoons$ ethyl-acetate and water.

This reaction can therefore take place from the left to the right as well as from the right to the left. When it takes place from left to right in the above instance, it proceeds only until two-thirds of the acetic acid and alcohol are converted.

If it occurs from the right to the left, it will also proceed to a certain equilibrium; and the noteworthy feature of a reversible equation is the fact that the same equilibrium is produced no matter which way the reaction takes place. The result will be the same in either case, whether we mix together a gram-molecule of alcohol and one of acetic acid, or a gram-molecule of ethyl-acetate and one of water.

In both cases, when the liquid reaches equilibrium, it contains

Two-thirds of a gram-molecule of ethyl-acetate
Two-thirds of a gram-molecule of water
One-third of a gram-molecule of alcohol
One-third of a gram-molecule of acetic acid.

The following are a few important reversible reactions:

Iron-oxide, when heated, is reduced by Hydrogen to form water and metallic Iron; but when water-steam acts upon metallic Iron at red heat, the reverse process occurs, Iron-oxide and Hydrogen being formed.

Carbon-monoxide and water-steam, when heated, form Carbon-dioxide and Hydrogen; if a mixure of Carbon-dioxide and Hydrogen is heated, steam and Carbon-monoxide are formed.

Chlorine and water act upon each other to form hypochlorous and hydrochloric acids; likewise, if hydrochloric acid and hypochlorous acid are mixed, Chlorine and water are formed.

If we add sulphuric acid to a solution of Sodium-chloride, the reaction is

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

Even this process is incomplete—it proceeds only to a certain limit. The product contains not only Sodium-sulphate and hydrochloric acid, but also some Sodium-chloride and sulphuric acid which have escaped the reaction.

The Sodium present is not sufficient to neutralise both the sulphuric and hydrochloric acids completely, and therefore the acids divide it between them—not equally, however, for the acid having the greater affinity for Sodium takes the larger part.

The various intensities with which different acids in the same solution take up a base is said to be their respective *avidities* for the base in question.

We determine the avidity of hydrochloric and sulphuric acids by determining the proportion of the quantities of Sodium which unite with each when the experiment is made according to the above equation.

The result is that 66.6 percent of the Sodium present unites with the hydrochloric acid, while the other 33.3 percent combines with the sulphuric acid. Hence the avidity of hydrochloric acid for Sodium is twice as great as that of sulphuric acid; or if the avidity of hydrochloric acid is taken as 100, that of sulphuric acid is only 50.

The following table gives the relative avidity of a few acids for Sodium:

Nitric acid	100
Hydrochloric acid	100
Hydrobromic acid	89
Hydroiodic acid	79
Sulphuric acid	50

As yet we have studied only instances where the reacting substances are used in quantities indicated by the chemical equations. In the case of acetic acid and alcohol, we supposed that when the reaction takes place from the left to the right 60 parts of acetic acid and 46 parts of alcohol were used; and when the reaction occurs in the opposite direction, 18 parts of water and 88 parts of ethyl-acetate were taken. But how would the equilibrium be influenced by an excess of one of the reacting bodies? We find that

An excess of one of the reacting bodies increases the decomposition of the other reacting bodies on the same side of the equation. It will therefore increase the quantities of the reaction products on the other side of the equation.

Suppose we mix 60 parts of acetic acid and 46 parts of alcohol and add some water (which is one of the reaction products); we find that

The addition of one of the reaction products to the reacting bodies decreases the degree of chemical change. Therefore, less ethyl-acetate and water are formed.

As the addition of one of the reaction products decreases the degree of the reaction, it is evident that if one of these be removed from the place of reaction in some manner, it will increase the degree of chemical change and finally make the reaction complete. For instance, if we mix 60 parts of acetic acid and 46 parts of alcohol and add to this something that will remove the water formed (concentrated sulphuric acid, Zinc-chloride, Calcium-chloride, etc.), the reaction will go on to completion and all the alcohol and acetic acid converted into ethyl-acetate. We can likewise reverse the reaction by mixing 88 parts of ethyl-acetate and 18 parts of water; part will form acetic acid and alcohol, and the reaction can be made complete

by adding something which will remove the acetic acid (an alkali, etc.). The completion of a chemical action can therefore be secured

1. *By increasing the quantity of one of the reacting bodies.*

2. *By the removal of one of the reaction products from the place of reaction.*

This can be brought about by

(a). A secondary reaction, as the addition of something which will combine with one of the reaction products.

(b). By reason of one of the reaction products being volatile.

The reaction which takes place between sulphuric acid and Sodium-chloride can be made complete (although the avidity of the sulphuric acid is but half that of the hydrochloric acid); for the hydrochloric acid has a far lower boiling point than the sulphuric acid, and continually evaporates—heat facilitating the process.

Then we may say that *all reaction are practically complete in which a gas is formed and not prevented from escaping.*

(c). By reason of one of the reaction-products being insoluble.

When solutions of Sodium-chloride and Silver-nitrate are mixed, Sodium-nitrate and Silver-chloride are formed;

$$NaCl + AgNO_3 = NaNO_3 + AgCl$$

Were all the products soluble, reaction would cease at a certain point; but as Silver-chloride is insoluble, it escapes from the place of reaction by being precipitated, and the equilibrium is disturbed—the precipitation of all Silver-chloride allowing the process to become complete.

The fact that not only the peculiar individual affinity of the factors but also their respective quantities and the presence of the reaction products greatly influence a chemical reaction, was brought to light by the french chemist Bertholet; it remained, however, for two norwegians to formulate this mathematically, and this important law is now known as the *Guldberg' and Waage's law of the chemical mass action.*

Chemical statics investigate the conditions of chemical systems in equilibrium, and the causes by which this equilibrium is changed.

Not only is chemical equilibrium under the influence of mass action, but the *reaction velocity* is also affected.

Entire reaction velocity is that with which the chemical process proceeds from the moment action commences until equilibrium is reached.

Reaction velocity is often very slow. When acetic acid and alcohol are mixed in proper proportions and let stand at ordinary temperature, many days elapse before equilibrium is reached.

A mixture of Oxygen and Hydrogen can be kept for years without any observable change; nevertheless, the system is not in equilibrium, the gases combining to form water at a very slow rate until equilibrium is attained.

That part of theoretical chemistry which investigates the reaction velocity and conditions which affect it, is known as *chemical kinetics.*

CHAPTER XV.

THE CAUSES OF CHEMICAL ACTION.

To bring about chemical action, certain impulses of a mechanical or physical nature are generally necessary—as change of pressure, concussion, rise of temperature, light, electricity, etc. These impulses are of various kinds:

1. *Condition* (*solid, liquid or gaseous*).

Chemical affinity is only evinced upon contact of the atoms or molecules. Gross bodies, therefore, exert very little chemical action upon each other, because their molecules do not intermingle. If they are powdered and then mixed, a far greater affinity is observed to operate; but, nevertheless, their reaction upon each other is still very weak.

The best medium for chemical action is the liquid condition. The great mobility of the molecules of liquids allow then to come in close contact with each other. If a liquid and a solid are brought together, the reaction is very much greater than if both were solids; and is still more energetic if both are liquids.

This influence of the liquid condition upon the occurrence of chemical action was recognised by the ancient scientists, as their saying, '*Corpora non agunt, nisi fluida*' proves.

In order to induce chemical action between solids, it is best to melt them or dissolve them in the same solvent separately, and then add the two solutions together.

The gaseous condition, although permitting the most perfect intermingling of the molecules, does not offer the inducement to chemical action that the liquid condition does, because gases are

not nearly so dense as liquids and their molecules do not therefore come in such intimate contact.

2. *Pressure.*

Pressure brings the molecules of a gas nearer together, and thus facilitates chemical action. A mixture of powdered solids can often be chemically combined by subjecting it to pressure; as Iron-powder and Sulphur-powder unite under a pressure of several thousand atmospheres and form Iron-sulphide.

3. *Concentration.*

When a solution is concentrated the dissolved molecules are brought closer together. The energy with which chemical activity takes place is thus affected by concentration.

4. *Heat.*

As explained, heat is the most powerful agent in chemical activity. It is universally employed for this purpose in all walks of life.

5. *Mechanical impulse* (*concussion, friction, etc.*)

Very energetic chemical action is often produced by friction or by concussion. Phosphorus matches are ignited by friction; fulminate of Mercury in percussion caps explodes by a blow; some chemicals (as Nitrogen-chloride, Chlorine-monoxide, etc.) explode even when gently touched.

Although many such reactions may be caused by the heat produced and therefore not be strictly mechanical actions, yet this is not so in all cases. For instance, dry Nitrogen-iodide is so explosive that the shock caused by the touch of a fly or the falling of a particle of dust may lead to an explosion.

Not any form of blow will bring about an explosion in the above-cited cases; nitro-glycerin may be very roughly handled and yet not explode, while the mechanical motion caused by the explosion of a small quantity of fulminate of Mercury, even at a distance, will induce explosion. The action of concussion is in some instances more powerful than that of heat. Dynamite and guncotton, if ignited, burn rapidly but quietly

and without explosion; if chemical action is brought about by percussion, however, the resultant explosion is terrific.

There is thus no doubt that it is possible to directly induce chemical change by mechanical means. All substances which are chemically affected by mechanical means, however, are endothermic, and therefore such reactions are always accompanied by the disengagement of heat.

6. *Katalytic action.*

In some instances where two substances react very slowly upon each other under ordinary conditions, their rate of action can be greatly increased by the introduction of a third substance which does not seem to participate itself in the chemical action.

This is illustrated in the action of porous Platinum (Platinum sponge or Platinum black) on a mixture of Oxygen and Hydrogen. This mixture can be kept indefinitely without change; but if a little Platinum black is added to it, the gases unite at once with an explosion—no change being remarked in the Platinum. Hydrogen may also be ignited in air by contact with porous Platinum.

Sulphur-dioxide (SO_2) does not unite with Oxygen at ordinary nor even at high temperatures; but their union is effected if they are passed over heated Platinum sponge.

In the above cases, the Platinum does not change itself, but causes the chemical action of the other bodies by its presence.

Chemical actions induced (or, more correctly, the velocity of which is altered) by a third body which remains itself unaltered, are *katalytic or contact reactions.*

A katalyser is a substance which, by its presence, alters the velocity of chemical action. Platinum sponge is the katalyser in the example given.

Many bodies besides Platinum act as katalysers.

In order to unite Carbon-monoxide with Chlorine gas, to form $COCl_2$, Phosgen gas, a mixture of both gases is passed over animal charcoal. The katalytic action of Platinum and charcoal can be explained by the porosity of these bodies. (See solution of gases in solids).

There are two classes of katalysers

Accellerating katalysers as exampled, and

Retarding katalysers—those which lessen the rate of chemical action.

In the foregoing instances a chemical union of two substances took place by katalytic action; but many chemical decompositions are originated by katalytic action. For example, Hydrogen-dioxide splits very slowly into water and Oxygen ordinarily;

$$H_2O_2 = H_2O + O$$

But by the contact of a suitable katalyser (powdered Gold, Silver, Platinum or Manganese-dioxide) this decomposition is very rapid. This action may be , perhaps, explained as follows:

Hydrogen-dioxide acts as an oxidising agent, forming water and an unstable oxide of the metal used as katalyser. These intermediary products are at once broken up into free Oxygen and the metal. This supposition is corroborated by the fact that if the oxide of the katalytic metal is added to Hydrogen-dioxide, not only the latter splits into water and Oxygen but the oxide also separates into the metal and Oxygen. Dioxide of Hydrogen, which is ordinarily an oxidising agent, acts therefore as a reducing agent when in contact with certain unstable oxides by inducing them to give up their Oxygen.

A good example of katalytic action is the effect of Manganese-dioxide in the preparation of Oxygen. If this is added to Potassium-chlorate from which Oxygen is obtained by the addition of heat, a far lower temperature is needed and the reaction is completed much more quickly than is the case if Manganese-dioxide is not present. It is assumed that during the action the Potassium-chlorate oxidises the Manganese-dioxide, forming the higher oxides of Manganese, which are more easily decomposed by heat than the Potassium-chlorate alone.

The katalytic action of water is remarkable. Many chemical processes cannot be performed or performed but slowly if no water is present. Carbon-monoxide, a gas generally considered as combustible, can only be ignited with great difficulty if an absolutely dry mixture of it with Oxygen is tested; while, if

a small quantity of water-vapor is present, it will ignite rapidly with an explosion. This may also be explained by the assumption of intermediary products. The Carbon-monoxide reduces the water-vapor, forming Carbon-dioxide and free Hydrogen;

$$CO + H_2O = CO_2 + 2H$$

This process occurs at a relatively low temperature. The Hydrogen liberated mixes with the Oxygen, forming a mixture of Oxygen and Hydrogen, which easily ignites.

Other examples of the katalytic action of water are:

Metals are not oxidised at ordinary temperatures in absolutely dry air; Phosphorus, Carbon, etc., do not burn at all or only very feebly, in dry air.

The organic ferments have important katalytic action. An example of a ferment is found in yeast, a living, unicellular plant, made up of round cells. If added to a diluted solution of sugar, it produces fermentation—the sugar being decomposed and alcohol, Carbon-dioxide and some other products of lesser importance being formed. It was long believed that this decomposition by ferments was a life-process of the cells; but recent investigations show that the cells produce a chemical substance, called an *enzyme*, which, acting as a katalyser, produces chemical action.

Enzymes seem to be related to albuminous bodies, although little of their true chemical nature is as yet determined. They are altered by heat, and the cells which produce them are killed when the temperature rises above a certain degree; therefore fermentation and enzymatic action cease when the temperature attains the requisite degree.

Enzymes are soluble in water, but differ in their ability to osmote through porous membranes — especially through membrane of the cell which produces them. Some are able to permeate the cell-wall and are found in the aqueous solution outside of the cell; on filtering the liquid containing the cells, enzymes of this nature are found in the filtrate. They are said to be *extra-cellular enzymes*. Pepsin in the gastric juice and trypsin in the pancreatic juice are extra-cellular enzymes.

Other enzymes, again, cannot osmote through the cell membranes, and the filtrate of a liquid containing the cells which produce them will be free of enzymatic action. These are *intra-cellular enzymes.* Zymase in the yeast cell is an example.

In order to obtain an intra-cellular enzyme in solution, the membrane of the cell must be mechanically destroyed by trituration with sand or glass powder, and the liquid contained in the cells pressed out. In modern chemical nomenclature, the ending *-ase* is used to designate an enzyme—as zymase, peptase, etc.

The chemical action of enzymes is to cause the substance upon which they act to take up water. The compound formed is very unstable, and breaks down into several decomposition-products. A decomposition in which a body combines with water and forms an intermediary compound (hydrate) which then breaks down into simpler substances is the process of *hydrolysis.* The action of enzymes is a hydrolytic action. Enzymes are further classified according to the substances upon which they act, as *amylolytic enzymes,* which decompose starch; *proteolytic,* which break down albuminous matter, etc.

Inorganic ferments or *enzymes.*

Through recent discoveries it has become possible to dissolve metals in water. In reality, solution of the metal is not brought about, but suspension in exceedingly fine particles in the water. This condition can be maintained for months without the metal settling to the bottom. The liquid appears transparent and can be filtered. The metal in such a solution is not able to osmote through porous membranes, and is therefore in a colloidal state. These liquids are called *colloidal solutions of metals* or *sols.*

The ending -sol is added to the name of the metal, as Platinsol, Argenti-sol (Silver sol), Auri-sol (Gold sol), etc.

There are several methods of preparing such solutions. One of them is to place the positive and negative electric poles, made from the metal of which the sol is desired, in a vessel containing absolutely pure water. The ends of the poles are then brought close together, but not in contact. As absolutely pure water is a non-conductor of electricity, the current passes in sparks

through the water and metallic particles are driven from the negative pole and will be suspended in the water, causing the formation of a sol.

These sols resemble enzymes very closely and are called *inorganic ferments.* They are powerful katalysers. The decomposition of Hydrogen-dioxide into water and Oxygen is greatly accellerated by them. Only very small quantities are necessary for katalytic action.

Colloidal Mercury and colloidal Silver are used in medicine.

7. *The nascent state.*

Some substances have far greater activity and are able to form compounds much more readily if they are brought together with other bodies at the moment of their own liberation from a compound. This is especially true of Oxygen. This condition is spoken of as the *nascent state.*

The explanation of this increased energy in the nascent state is usually given as follows:

The molecules of nearly all elements consist in the free state of more than one atom. If an element in a free state combine with another body, it is evident that in order to do so the atoms constituting its own molecule must be severed. For this cleavage energy is required; but this is not the case with a nascent body, which is already separated and can act directly upon other bodies. This explains why many bodies do not oxidise in air, but are easily oxidised when treated with substances rich in Oxygen: the energy required to split Oxygen atoms from these oxidising agents being less than that required to break up the molecule of Oxygen.

Active and passive condition of elements.

In a like way the so-called *active condition* of an element is explainable. Oxygen occurs in two different modifications; the *common* or *passive Oxygen* and the *active Oxygen* or *Ozone.* Passive Oxygen acts very feebly upon other bodies at ordinary temperatures, while ozone is a very powerful oxidising agent. The specific gravity of Ozone is just one and a half times that of Oxygen, hence if the molecule of common Oxygen consists of

two atoms, and its formula is O_2, the molecule of Ozone consists of three atoms and has a formula of O_3. The Ozone molecule is very unstable, and breaks down easily into a molecule of Oxygen and an atom of the same

$$O_3 = O_2 + O$$

Hence if Ozone acts upon other bodies, the liberated Oxygen atom can unite directly with them; while, when ordinary Oxygen acts, its molecule must be first split into two atoms, and this requires a larger amount of energy than the former process.

8. *Light.*

The production of chemical action by light is of great importance. Photography is based upon it; linen and cotton bleaching is effected by exposure to sunlight. Colors, especially anilin dyes, are faded by sunlight; a mixture of Chlorine and Hydrogen will explode in direct sunlight, while in modified light the gases unite slowly to form hydrochloric acid. Many chemicals (Silver salts, Gold salts, organic preparations, etc.) must be kept in dark places, or they will decompose. The formation of starch in the green parts of plants only occurs in light. This last is of such great importance that life on earth depends upon it. Plants convert the Carbon-dioxide of the air into starch by the energy of the sun's rays, and furnish in turn the food for animals. Thus all life on our earth may be said to be produced by the action of sunlight.

Actinic action is the technical term for the chemical effect of light.
Light rays causing chemical action are called *actinic rays.*

White sunlight is composed of a great number of rays, which have different wavelengths. If sunlight is allowed to pass through a prism, a spectrum is formed. The different rays composing the light are differently refracted by the prism, and when they leave it each continues in the angle to which it has been bent in the prism. As each of the different rays carries a characteristic sensation to the sense of vision, the spectrum is seen to consist of a band of different colors. These are red, orange, yellow, green, blue, indigo and violet. Beyond the red on the one end and the violet on the other, the spectrum still

extends—although not visible to the human eye. These portions are the infra-red and ultra-violet parts of the spectrum. The existence of the infra-red extension can be proven by its action on a very sensitive instrument for measuring temperature; and that of the ultra-violet part by its action upon a photographic plate.

Rays having chemical effect are in all parts of the spectrum. The popular belief that only the blue, violet and ultra-violet rays are able to produce chemical activity is erroneous.

The false impression is obtained in the study of photography, although the most active rays here are really those of the blue, violet and ultra-violet. In some other instances red light is the more energetic. An aqueous solution of Hydrogen-sulphide is more quickly decomposed by red light than by any other. For the formation of starch in plants, the yellow and orange are the most effective, next the green and red rays.

Thus the power of the rays of light differ with the chemical process in which they are engaged.

9. *Electricity.*

As electricity has an important effect upon chemical action, we will treat of it in the next chapter separately.

CHAPTER XVI.

Volta, Davy, Becquerel, Berzelius and others showed that electricity is often produced when a chemical action takes place. One of the principal sources of electricity is chemical action, as seen in the galvanic battery; and electricity from chemical energy is called *chemical, galvanic* or *voltaic electricity*—after the italian scientists Galvani and Volta who discovered and studied it.

Electricity, in turn, produces chemical effects. If an electric current is passed through a solution of a salt, a chemical decomposition occurs; the metal being deposited on the negative pole. Water is split by electricity into Oxygen and Hydrogen; hydrochloric acid into Hydrogen and Chlorine.

Electro-chemistry treats of the relation between chemical and electrical phenomena.

To the electrician, there are two great classes of bodies:

1. *Conductors*—those which allow of the passage of electricity through their substance.
2. *Non-conductors—or isolators*—which do not show electricity in all parts if connected with an electric current.

This distinction is not absolute, for the best conductors offer more or less resistance to the passage of electricity; and there is no insulator so perfect but that it will conduct some electricity.

The quantity of resistance is measured by the *ohm*—this being the resistance of a Mercury column having a trans-section of one square millimeter and a length of 106.3 centimeters at 0° C.

Conductors are again divided into two classes:

1. *Conductors of the first class or metallic conductors* are those which conduct electricity without being themselves chemically changed; the metals belong to this class, as does also gas-carbon.

2. *Conductors of the second class*—those which undergo chemical change when an electric current is passed through them (acidulated water, hydrochloric acid, solutions of Copper-sulphate, etc. etc.).

Electrolysis is the chemical decomposition brought about by passing an electric current through a body.

An electrolyte is a conductor of the second class.

Electrolytic conductivity is that which is accompanied by simultaneous chemical change. Electrolysis differs from other chemical decomposition in that the deposit of the products is localised to the two poles dipped in the electrolyte. The positive pole is called the *anode;* the negative is called the *katode.*

The electrolyte is split into two components, which are called *ions;* and these deposit one at the anode (this is the *anion*) the other at the katode (this is the *kation*). As bodies attract only those other bodies which are charged with an opposite electricity to their own, the anion, which is attracted by the anode, must be charged with negative electricity; and the kation, which is attracted by the katode, must be charged with positive electricity.

The negative ion (anion) is indicated by the sign (—) placed over the formula; while the positive ion (kation) is indicated by the sign (+). Thus the electrolysis of hydrochloric acid is expressed by the following electro-chemical equation:

$$HCl = \overset{+}{H} + \overset{-}{Cl}$$

The equation for the decomposition of nitric acid is

$$HNO_3 = \overset{+}{H} + \overset{-}{NO_3}$$

Evidently a distinction must be made between simple ions, as H and Cl, and compound ions, as NO_3. If a chemical compound consisting of more than two elements is subjected to electrolysis, it splits into but two ions—of which one or both are compound ions.

If a compound which contains several ions of the same kind (as sulphuric acid, H_2SO_4, which contains two positive hydrogen ions) is split into its ions, it is evident that the sum of the magnitude of the electrical charges of the positive ions will be equal to the sum of the electrical charges of the negative ions; because both together have been formed from the electrically inactive sulphuric acid molecule, in which the positive and negative neutralised each other. The electro-negative charge of the SO_4 ion, then, equals in magnitude the electro-positive charges of two Hydrogen ions; or is twice as great as the positive charge of one Hydrogen ion. This is usually indicated by two minus signs (— —) placed over the formula:

$$H_2SO_4 = \overset{+}{H} + \overset{+}{H} + \overset{=}{SO_4}$$

Hence each — sign over the symbol of an ion indicates a negative charge equal in magnitude to the positive charge of one Hydrogen ion. Each + sign over the symbol of an ion indicates a positive charge equal to that possessed by an ion of Hydrogen.

Besides this primary decomposition of an electrolyte into ions, secondary chemical processes are also observed, caused by the action of the ions upon the solvent or on the material of which the electrodes are composed. The following example will demonstrate this secondary action:

If an electric current is passed through a solution of Potassium-sulphate, the primary reaction is

$$K_2SO_4 = \overset{+}{K} + \overset{+}{K} + \overset{=}{SO_4}$$

But both the kation, K, and the anion, SO_4, are acted upon by the water contained in the solution, thus:

$$K + H_2O = KOH + H$$

and

$$SO_4 + H_2O = H_2SO_4 + O$$

Hence, at the negative pole, instead of metallic Potassium, Potassium-hydrate and Hydrogen are formed; while at the positive pole sulphuric acid and free Oxygen are produced.

Farraday's law:

When the same electric current is passed through various vessels, each containing a different electrolyte, the quantities deposit ed on the poles during an equal time are proportional to the chemical combining weights:

If the electrolytes arranged in series are

1, nitric acid. 2, Copper-nitrate. 3, Silver-nitrate. 4, Lead-nitrate. 5, Bismuth-nitrate. Then the quantities of Hydrogen Copper, Silver, Lead and Bismuth which are deposited at the negative poles bear the ratio

H, 1 : Cu, 31.5 : Ag, 108 : Pb, 102.67 : Bi, 69

or the ratio of their combining weights.

This law is therefore employed to determine the combining weights.

As the combining weight of an element is equal to its atomic weight divided by its valence, the law may also be expressed, according to Helmholtz,

When the same electric current passes through different electrolytes for the same length of time, the same number of valences are invariably solved.

Thus if a current is able to split one molecule of Aluminum-chloride, $AlCl_3$, and solve three bonds, it will be able to split $1\frac{1}{2}$ molecules of Copper-sulphate, $Cu{=}SO_4$, each molecule of which has two bonds to solve; and three molecules of Silver-nitrate, $Ag.NO_3$, which has but one bond.

An electro-chemical molecule (Kohlrausch) is a chemical molecule divided by the number of valence-bonds which combine the anion with the kation. Hence the mass of an electro-chemical molecule of sulphuric acid, H_2SO_4, equals the molecular mass (98) divided by two, as two bonds unite the anion and kation.

According to this definition of an electro-chemical molecule, we may express Faraday's law as follows:

All electro-chemical molecules, regardless of their chemical condition, require the same quantity of electricity for their decomposition.

This law of Faraday seems to contradict all other facts collected by chemical observation and experiment. According to it, the same quantity of electricity solves the valence which connects the Hydrogen and the Chlorine in hydrochloric acid, and also the valence which connects the Hydrogen and the Iodine in hydroiodic acid. But thermo-chemical and other measurements show that the union between the Hydrogen atom and the Chlorine atom is far firmer than that between the Hydrogen and the Iodine atom; and that a far greater amount of energy is required to split hydrochloric acid than is required to split hydroiodic acid. We might logically assume that a greater amount of electricity will also be required for the same work; but Faradays law contradicts this, and necessitates an explanation of this and the following phenomena.

There is no substance which at ordinary temperature and in an absolutely pure state will act as an electrolyte. Pure water does not conduct electricity, nor do pure hydrochloric acid gas gas or a sulphuric acid of 100 percent. As soon, however, as the hydrochloric acid gas is dissolved in water or the sulphuric acid mixed with water, liquids are obtained which are very good conductors. There is evidently some action of the water upon the acids. These peculiarities are emphasized if we study the relation between the concentration of a solution and its electrolytic conductivity. As is to be expected, the conductivity is increased by a greater concentration—though not in proportion to the concentration. *Concentrated solutions have a relatively smaller degree of conductivity.*

Another phenomenon of aqueous solutions not in harmony with the laws studied in the chapter on solutions, is the depression of the freezing point and the elevation of the boiling point undergone by water when electrolytes are dissolved in it. The magnitude of the depression and elevation increases with the concentration here also, but not proportionally to the concentration. More highly concentrated solutions of electrolytes have

not relatively so large a depression of the freezing point or elevation of the boiling point as the concentration would seem to warrant.

If a gram-molecule of any substance which is not an electrolyte is dissolved in 100 grams of water, the freezing point depression is always18.6°, as we have seen. This is the case in aqueous solutions of sugar and of urea; but in aqueous solutions of electrolytes the freezing point depression and the elevation of the boiling point are relatively greater. When one gram-molecule of Sodium-chloride (NaCl = 58 grams) is dissolved in 1000 grams of water, the depression of the freezing point is 3.72°; that is, 2 x 1.86. When a gram-molecule of Calcium-chloride ($CaCl_2$ = 111 grams) is dissolved in 1000 grams of water, the depression is 3 x 1.86 or 5.58° C. When a gram-molecule of Aluminum-chloride ($AlCl_3$ = 133.5 grams) is dissolved in 1000 grams of water, the depression is 4 x 1.86 or 7.44° C. It seems, therefore, as if the solution of Sodium-chloride contains twice as many, that of Calcium-chloride three times as many and that of Aluminum-chloride four times as many gram-molecules of the dissolved substance as were taken; or as if the molecule of Sodium-chloride has split into two simpler molecules, that of Calcium-chloride into three and that of Aluminum-chloride into four when dissolved in water. These apparent vagaries are all explained by a hypothesis first advanced by Clausius and later developed to a theory by Swante Arrhenius,

The theory of electrolytic dissociation.

According to this theory, electricity is not required to split the electrolyte into ions—the water does this. This property of water (and some other liquids) is their *dissociating power.*

This dissociation of an electrolyte, caused by solution in water, does not occur suddenly or affect the whole quantity of the dissolved substance at once. If the solution is highly concentrated, the number of molecules which undergo dissociation is but small; but the addition of increasing quantities of water causes more and more molecules to dissociate, and this dissociation is theoretically complete only when the quantity of water is infinitely large. The free ions behave as molecules. Hence a solution of one molecule of Sodium-chloride (NaCl) when

completely dissociated, contains two ions; a solution of one molecule of Calcium-chloride ($CaCl_2$) three ions; and a solution of one molecule of Aluminum-chloride ($AlCl_3$) four ions—which act as independent molecules in each instance and cause depressions of the freezing points or elevations of the boiling points which are two, three or four times as great as if the molecules of these compounds were not split.

This theory also explains why a concentrated solution, not fully dissociated, has a relatively smaller depression of the freezing point and elevation of the boiling point.

When the diluted solution is evaporated, the dissociated particles gradually reunite and form the original molecules, and this process is completed when all water is evaporated.

Then the electrolytic dissociation is a reversible process and may be expressed as follows:

$$CaCl_2 = \overset{+\,+}{Ca} + \overset{-}{Cl} + \overset{-}{Cl}$$

The ions move in the liquid in all directions in zig-zag lines, according to the kinetic theory of solutions. If the poles of a battery are introduced and an electric current passed through such a solution, the motion of the ions is regulated to certain lines, and under the influence of the current the positive ions move to the negative pole and the negative ions to the positive pole. This is the *migration of the ions.*

Reaching the electrodes, the ions discharge their electricity and become electrically inactive. It is not the electric current which splits the substance into ions, but the act of solution; the electrodes attract all different ions charged with an equal amount of electricity alike. This theory conforms with Faraday's law.

The irregularities of the electric conductivity of solutions can also be explained by this theory. Instead of the molecule of the undissociated substance being the conductor of electricity, it is the free ions that do this. As a concentrated solution is not dissociated into ions to the extent that a diluted solution is, it has a relatively smaller degree of conductivity.

The degree of electrolytic dissociation is the ratio of the quantity dissociated to the total quantity of the original substance taken.

If we dissolve 100 grams of Sodium-chloride in water and 10 grams dissociate, then the degree of dissociation is 10 percent.

The experimental methods for determining the degree of electrolytic dissociation are based upon (a)—the determination of the osmotic pressure; (b)—the depression of the freezing point; (c)—the elevation of the boiling point; and (d)—the determination of the electric conductivity.

Color of ions.

If water possesses the power to split salts, acids and bases into ions, we are led to expect that the color of a diluted aqueous solution is the color of the ions. Suppose that Sodium-chloride is dissolved in water, it seems logical to conclude that this will show the properties of Sodium, which is a Silver-like metal, and Chlorine, which is a greenish gas; but this is not the case—the solution is colorless. The reason for this is easily understood. The assumption that the properties of the ions are the same as the properties of the elements is erroneous. *First,* the molecules of most elements consist of more than one atom, the properties of an element as usually described (color, brightness, etc.) refer to the molecules and their arrangement; of the physical properties of the single atoms we are entirely ignorant. *Second,* there is difference between atoms and elementary ions—between Chlorine ions and atoms of Chlorine, because ions are electrically charged and atoms are not and the properties of ions are modified by the nature of the charge they carry.

For instance, there are two different kinds of Iron ions, Ferrous and Ferric. Both consist of one atom of Iron, but the magnitude of their charges is different:

$$\text{Ferrous-chloride, } FeCl_2, = \overset{++}{Fe} + \overset{-}{Cl} + \overset{-}{Cl}$$

$$\text{Ferrric-chloride, } FeCl_3, = \overset{+++}{Fe} + \overset{-}{Cl} + \overset{-}{Cl} + \overset{-}{Cl}$$

This different electric charge makes the Ferrous ions (green) to appear different to the Ferric ions (brown).

From the fact that the solutions of the Sodium and Potassium salts of hydrochloric, sulphuric, nitric and other acids are colorless, we draw the conclusion that the following negative ions are devoid of color:

Colorless negative ions.

Cl, Br, I, F, SO_4 (sulphate), SO_3 (sulphite), S_2O_3 (thio-sulphite), NO_3 (nitrate), NO_2 (nitrite), PO_4 (phosphate), AsO_4 (arsenate), P_2O_7 (pyro-phosphate), CO_3 (carbonate), OH (hydroxyl), CH_3COO (acetate), ClO_3 (chlorate).

From the color of the diluted aqueous solutions of the Sodium salts, we deduce the colors of the following

Colored negative ions.

CrO_4 (chromate), yellow; Cr_2O_7 (dichromate), orange-red; MnO_4 [— —] (manganate), green; MnO_4 [—] (permanganate) violet.

Therefore, although the formulae of the ions of the manganate and permanganate are identical, the color of their ion is different because they carry different charges of electricity.

Colorless positive ions.

H, Na, K, Li, NH_4, Ag, Ca, Ba, Sr ,Mg, Zn, Pb, Hg, Al.

Colored positive ions.

Cu, blue; Fe (Ferrous), green; Fe(Ferric), brown; Ni, green; Co, red; Au, yellow; Pt, brown.

Knowing the colors of the different ions, we are able to compute the color of any diluted aqueous solution of acids, bases or salts. Even the color of the solid salts, if they are soluble in water, can usually be determined from the color of the ions of which they are composed; because, even in the solid state, some of the electrolyte is ionised. This explains the fact that all salts which contain the same positive but different colorless neg-

ative ions have the same color. All Copper salts are blue, all Ferric salts are brown, all Potassium salts are colorless unless the negative ion imparts a different color. In a few instances the solid may not have the expected color—Copper-chloride is yellow; but if this is dissolved in a large enough quantity of water, the solution becomes blue by the complete ionisation of the Copper salt, while its concentrated solution is green because it is only partly dissociated and the blue Copper ion and the yellow molecule of Copper-chloride mix (blue and yellow form the green color).

Only those salts which are insoluble in water have colors which cannot be computed from the ion-colors. Lead-iodide, Silver-phosphate, Silver-iodide, Mercurous-iodide are yellow and Mercuric iodide is red, although they are composed of colorless ions—these salts are insoluble in water.

Chemical properties of ions.

The chemical properties and reactions of an electrolyte are due to the ions:

1. *Acids.* The common properties of all acids are due to the positive Hydrogen atoms dissociated by solution. An acid can therefore act only as such when dissolved in a solvent which has dissociating power. Absolutely dry hydrochloric acid gas does not affect litmus paper, and if dissolved in chloroform the solution obtained does not conduct electricity and is therefore not ionised—nor does it affect Calcium-carbonate. As soon, however, as a trace of water is added, it turns blue litmus paper red and acts energetically upon Calcium-carbonate, causing it to effervesce.

According to the theory of electrolytic dissociation, the reacing power of an acid depends upon the number of free Hydrogen ions in a given volume. The greater the number of these ions, the greater the reacting power of an acid.

As the gram-equivalent of an acid is that quantity which contains one replaceable gram of Hydrogen, it is evident that equivalent quantities of all acids when so diluted that all molecules are dissociated, will contain the same number of Hydrogen ions; therefore *equivalent quantities of all acids, when properly dilu-*

ted, have the same intensity of reaction. This is not so when the dilution is not sufficient to complete dissociation. The degree of dissociation which a gram-equivalent of an acid undergoes when dissolved in a limited quantity of solvent, differs for different acids. Hence in more concentrated solutions *those acids are stronger which dissociate more easily into ions; and the degree of dissociation which an acid undergoes on the addition of a limited amount of water is a measure of its chemical strength.*

As degree of dissociation can be measured by the electric conductivity, the acids, when tabulated according to their chemical strength, have the same order as when they are arranged according to their electric conductivity. Acids can therefore be classified as follows:

(a) *Strong acids*—those which are largely dissociated; that is, more than 50 percent in a normal solution (sulphuric, hydrochloric, nitric, hydrobromic, hydroiodic, etc.).

A normal solution ($\frac{N}{1}$) of a substance contains one gram-equivalent dissolved in a liter.

(b). *Moderately strong acids*—those which are dissociated 10 percent or somewhat more in a normal solution (phosphoric, acetic, etc).

(c) *Weak acids*—those which dissociate but little (boric, carbonic, etc.).

2. *Bases.* According to the theory of electrolytic dissociation a base is a substance which forms in aqueous solutions negative OH ions; the active part of a base is this OH ion. It is evident that the base will be stronger the more free OH ions are present in a certain quantity. It follows that

(a). *Equivalent quantities of all bases, when dissolved in a very large quantity of water, possess each equal strength, because they contain the same number of OH ions.*

(b). *Bases dissolved in a quantity of water not sufficient*

for complete dissociation are stronger in proportion as they undergo a greater degree of dissociation.

3. *Neutralisation.* In all chemical reactions, according to the dissociation theory, *the tendency of the electro-chemical forces is to produce electro-neutral molecules which have a lesser degree of dissociation than the molecules of the factors acting.*

This law is of fundamental importance, and explains all chemical reactions—as neutralisation, precipitation, etc.

Water dissociates but little; hence, if positive H ions and negative OH ions are present in a mixture, they will unite when they collide with each other and form the electro-neutral molecule of water (H_2O). The same occurs in the process of neutralisation when an acid and a base are mixed.

The acid partially dissociates

$$HNO_3 = \overset{+}{H} + \overset{-}{NO_3}$$

Then the bas

$$KOH = \overset{+}{K} + \overset{-}{OH}$$

Now the Hydrogen ions combine with the OH ions

$$\overset{-}{OH} + \overset{+}{H} = H_2O$$

If the three equations are added, the process may be expressed

$$HNO_3 + KOH = \overset{+}{K} + \overset{-}{NO_3} + H_2O$$

As the H ions and the OH ions which are dissociation products of the nitric acid and Potassium-hydroxide dissappear as such from the place of reaction when they unite, then according to the law of chemical mass action further parts of the acid and of the base are caused to split into ions. This process is repeated until all electro-neutral molecules of the acid and base are split and the liquid, as it does not contain any free H or OH ions, is neutral. The resultant liquid contains only electro-neutral water molecules and positive K and negative NO_3 ions; which latter, if the concentration is great, unite and form electro-neutral molecules of KNO_3.

Theory of indicators.

An indicator is a substance extremely sensitive to the presence of acids or alkalies, which it indicates by a change of color.

Litmus is an indicator.

The action of indicators is explained by the electrolytic dissociation theory as follows:

(a). Indicators are very weak electrolytes, either acid or basic. When dissolved in water, their dissociation is extremely meagre; the acid indicators form few positive H ions, the basic few OH ions.

(b). The color of the electro-neutral molecule of an indicator is decidedly different from the color of the second ion which is split off.

Let us now follow the action of an acid indicator—say phenolphthalein. Its electro-neutral molecule is white, and therefore it is a white powder. This is but little soluble in water, and its aqueous solution is only dissociated in slight degree, forming few positive H ions and a few negative ions which we may symbolise Ph. Hence the dissociation takes place thus:

$$\underset{\text{white}}{PhH} = \underset{\text{red}}{\overset{-}{Ph}} + \overset{+}{H}$$

Although the negative Ph ions have an intense red color, the solution of the substance in water is colorless because the dissociation is so weak that not sufficient Ph ions are freed to produce a coloration. But as soon as an excess of an alkali is added, forming OH ions, the few H ions split off from the Phenolphthalein unite with the OH ions and form water. According to the law of mass action the removal of the H ions from the place of reaction induces a fresh portion of phenolphthalein to dissociate. The number of free negative Ph ions in the liquid are finally increased sufficiently to color the solution a deep red.

If an acid is now added, the number of positive H ions in the liquid are increased greatly, because the acid frees them. But this reverses the dissociation of the phenol-phthalein, and the red negative Ph ions unite with the positive H ions and

form electro-neutral, colorless phenol-phthalein molecules. The red color thus disappears on the addition of an excess of acid.

The action of basic indicators may be explained in like manner.

5. *Precipitation.* Chemical reactions where an insoluble substance is precipated by an exchange of the basic and acid constituents of the salts, are also accounted for by the dissociation theory. Suppose a solution of Silver-nitrate is mixed with a solution of Sodium-chloride, a white precipitate of Silver-chloride is formed

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

This is practically a complete reaction. Applying the dissociation theory,

The Silver-nitrate is partially dissociated

$$\text{(a).} \qquad AgNO_3 = \overset{+}{Ag} + \overset{-}{NO_3}$$

The Sodium-chloride is also partially dissociated

$$\text{(b).} \qquad NaCl = \overset{+}{Na} + \overset{-}{Cl}$$

If both solutions are mixed, the mixture contains positive Ag ions, negative NO_3 ions, positive Na ions and negative Cl ions, in addition to the portions of undissociated $AgNO_3$ and undissociated NaCl. The different ions, moving in the mixture in all directions, will collide; and if two ions charged with opposite electricity are able to form an electro-neutral molecule of lesser degree of dissociation, they will do so—especially if the newly-formed molecule is insoluble, as insolubility pre-supposes a small degree of dissociation. Therefore when a positive Ag ion collides with a negative Cl ion, the electro-neutral molecule AgCl is formed, which is insoluble in water; and, as it precipitates, the number of free Ag and Cl ions in the liquid decreases. This results, according to the law of mass action, in a further dissociation of the electro-neutral molecules of $AgNO_3$ and NaCl and the process repeats until dissociation is complete.

The study of chemical analysis shows that tests for a base or an acid hold good for all its salts. For instance, all Lead salts

are precipitated by sulphuric acid; all chlorides are precipitated by Silver-nitrate. This is remarkable, as each chemical has its own peculiar properties, differing from those of the elements it contains. Lead-nitrate and Lead-acetate might be expected to have different properties from their respective components; sulphuric acid, however, gives a white precipitate with both.

Good reason for this, however, is shown by the theory of dissociation. Every Lead salt, when dissolved in water, frees Lead ions, and every sulphate in aqueous solution frees SO_4 ions; these, uniting, form the Lead-sulphate which is the precipitate of the tests mentioned.

This also explains why not all Chlorine compounds are precipated by Silver-nitrate. Chloroform, though it contains Chlorine, does not give the test because it is not an electrolyte and does not dissociate; and this occurs in many other instances.

6. *Hydrolysis. Reaction of normal salts.* Water dissociates, but in small degree. It has been determined experimentally that in 12½ million liters of pure water, about 18 grams are dissociated.

If a salt is dissolved in water, not only the salt is dissociated, but also some of the water. There are therefore four kinds of ions in the solution—two from the salt, and H and OH from the water. The ions formed from the water often participate in the reaction; such reaction is *hydrolysis* or *hydrolytic cleavage.*

A solution of Potasium-cyanide contains positive K ions, negative CN ions, positive H ions and negative OH ions. In moving through the liquid, some of the CN ions will collide with the H ions and form HCN (hydrocyanic acid); and some of the K ions will collide with the OH ions and form KOH (base). Thus by hydrolysis a solution of a salt always contains some free acid and some free base. Such hydrolytic processes can be expressed

(a). $KCN + H_2O = KOH + HCN$

(b). $K_2CO_3 + 2H_2O = 2KOH + H_2CO_3$

(c). $Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3H_2SO_4$

(d). $KNO_3 + H_2O = KOH + HNO_3$

The reaction upon an indicator can be then explained by the fact that the acid formed by the hydrolysis of the salt partially dissociates and forms free H ions, and the metallic hydroxide dissociates and forms free OH ions. Hence if the degree of dissociation of the acid and of the base are about the same, the liquid will contain an equal number of H and OH ions and the reaction will be neutral (d); but if the acid formed is weaker than the base formed, the dissociation of the acid is less than that of the base and there will be a smaller number of H ions than of OH ions and the reaction will be alkaline. This is the case in examples (a) and (b), where the acids formed have a far lesser degree of dissociation than the strong base, KOH. If the acid has a high degree of dissociation (as sulphuric acid in c), while the base formed has relatively a much smaller one, it is evident that the liquid will contain more free H ions, which produce a strong acid reaction.

The taste of solutions, the medical action of salts, acids and bases and many other phenomena are rendered intelligible by the electrolytic dissociation theory.

CHAPTER XVII.

THE PERIODIC LAW.

The following methods are extant for the classification of the elements:

1. According to their physical properties—metals and non-metals.

2. According to the chemical nature of their oxides—acid or basic.

3. According as to whether they unite with Hydrogen or not.

4. According to their electrical status—electro-positive and electro-negative.

All attempts to divide the elements according to these methods show many discrepancies. They merely illustrate that a dualism exists. If a list of all elements is made, beginning with the most metallic, electro-positive and base-forming one and terminating with the most decidedly non-metallic, electro-negative and acid-forming one, the elements gradually merge into each other; and those midway may sometimes be placed in one category, sometimes in the other.

5. Classification according to the valence and oxide formulae results in eight classes:

$$E_2O, \quad E_2O_2 \ (EO), \quad E_2O_3,$$
$$E_2O_4 \ (EO_2), \quad E_2O_5, \quad E_2O_6 \ (EO_3),$$
$$E_2O_7, \quad E_2O_8 \ (EO_4).$$

This classification is also faulty, as the valence varies and most elements form more than one oxide. To standardise this, the elements are classed according to their *highest* oxide which is either

acid or basic. Even when this is done, elements are often brought into the same class which according to most of their properties do not belong there.

Mendeljeff and Lothar Meyer discovered the law that all the properties of an element, physical and chemical, depend upon its atomic mass. The atom mass of an element is its one invariable property. All other properties (color, condition, melting point, boiling point,solubility, valence, etc.) are subject to change.

An advance toward the discovery of the law of atomic mass periods was made when certain regularities of the atomic masses of elements belonging to the same group was remarked. The german chemist, Doebereiner, pointed out the fact that, of the atomic masses of three elements in the same group, one is approximately the mathematical mean of the other two.

The atomic mass of Lithium is 7, that of Sodium is 23 and that of Potassium is 39; all three belong to the same group and form oxides of the general formula E_2O. The atomic mass of Sodium, 23, is seen to be the exact mathematical mean of the other two. The same is observed in the case of Calcium (40), Strontium (87) and Barium (136), which show a slight, but not important, deviation. Turning to Sulphur (32), Selenium (78.6) and Tellurium (126.6), we find a similar arrangement.

These divisions of three elements are named after their discoverer *Doebereiner's triades*. The remarkable fact about these triades is that the chemical and physical properties of the element standing midway are the mean of the properties of the two extremes. For instance, the specific gravity of Calcium is 1.57; of Strontium, 2.54; of Barium, 3.75. The specific gravity of the constituents of the Sulphur triade is: Sulphur, 2.04; Selenium, 4.6; Tellurium, 6.04. The specific gravity of the Chlorine triade (when solid) is: Chlorine, 1.33; Bromine, 3.15; Iodine, 4.95. The melting point of the Lithium triade are: Lithium, 180°; Sodium, 96°; Potassium, 58°.

And so all the other properties of the elements of a triade can be shown to correspond with their position; that is, to depend upon their atomic mass. The chemical properties of the elements of a triade sustain the same relationship to one another. The Chlorine triade become less negative as the atomic mass in-

creases—Chlorine being the most negative, Iodine the least and Bromine standing midway between the two.

This dependence of properties upon atomic mass is also seen in the analagous compounds formed by members of a triade. Of the sulphates of Calcium, Strontium and Barium, that of Calcium is the most soluble in water (although this is but slightly soluble), that of Strontium is less soluble and that of Barium is insoluble. Of the hydroxides of these elements, that of Calcium is least soluble in water, that of Barium most soluble, and that of Strontium again stands midway.

The dependence of the properties of elements upon the magnitude of their atomic masses has been known since the time of Doebereiner; but not until recent years was this knowledge applied to a systematic arrangement of the atomic masses of all elements by the immortal work of Mendeljeff and Lothar Meyer.

To comprehend the law they formulated, it is well to arrange the elements in a table, commencing with the one having the smallest mass—Hydrogen—and continuing in regular order through the increasing atomic masses; as Hydrogen (1), Lithium (7), Beryllium (9), Boron (11), etc.

This table is divided in such a manner that each division commences with an element belonging to the same natural group.

Suppose we select the group of alkali metals — Lithium, Sodium, Potassium, Rubidium and Cæsium—which are strikingly similar in chemical and physical properties. Commencing the first series with Hydrogen, and beginning a new series every time we encounter a member of this group, we obtain an arrangement similar to that in the table on page 218

The third series.

Let us now study more closely the third series of this classification—the chemistry of the elements contained in this division is probably more readily understood by the beginner. It comprises elements of the greatest importance; Sodium, Magnesium, Aluminum, Silicon, Phosphorus, Sulphur, and Chlorine.

If we consider the formulae of the oxides, by which we have

previously classified the elements, we meet at the outset with the fact that each member of this series belongs to one of the first seven groups; and arranged in the regular order of these formulae, they read:

E_2O (Sodium)	E_2O_2 (Magnesium)	E_2O_3(Aluminum)
E_2O_4 (Silicon)	E_2O_5 (Phosphorus)	E_2O_6 (Sulphur)
	E_2O_7 (Chlorine)	

Is it not wonderful indeed that, when the elements are arranged according to their atomic weights, they present the same order as the formulae of their oxides show? In searching for an explanation of this, the only reasonable hypothesis is that the oxide formulae result from the position of the atomic masses of the elements in the series; that, as the atomic mass of Phosphorus (31) places it between the atomic masses of Silicon (28) and Sulphur (32), its oxide formula must be between the oxide formula of Silicon (E_2O_4) and that of Sulphur (E_2O_6) orE_2O_5.

Not only the chemical properties mentioned are relative to the position of the element in this table, but all other chemical properties also. Sodium is an extremely positive element, and basic; Magnesium is quite positive, but less so than Sodium; Aluminum, although positive and basic, has a hydroxide which forms a weak acid and this element connects the positive, basic elements and the negative, acid-forming elements, Silicon, Phosphorus, Sulphur and Chlorine.

Whether an element is basic or acid-forming, electro-negative or electro-positive, metal or non-metal, is therefore dependent upon the atomic mass. We will see later that the physical properties are also determined by this.

The second series.

Lithium, Beryllium, Boron, Carbon Nitrogen, Oxygen and Fluorine.

Taking up the second series, we find them to agree in every other particular with their arrangement in the table. The formulae of their highest oxides being similar to the corresponding members of the third series. The seventh and last member, Fluorine (although it forms no oxide F_2O_7, because it does not

combine at all with Oxygen), substantiates, by the analogy of its compounds with those of Chlorine its position as seventh of the second series—even as the seventh position of the third series is occupied by Chlorine.

This series begins with the strongly-positive, basic metal, Lithium; Beryllium is strongly positive and basic, but less so than Lithium; Boron is a weakly-negative, acid-forming non-metal; and each following member of the series becomes more negative, acid-like and non-metallic in the order Carbon, Nitrogen, Oxygen, until the extreme is reached in Fluorine. The second series confirms the relation of the properties, chemical and physical, of an element to the position in the atomic mass series.

The difference between the atomic masses of two elements in the same group (having identical oxide formulae) is approximately 16, as an examination of the second and third series will show. Therefore if the elements are arranged in the order of their increasing atomic masses, the characteristic properties of a member of a series will repeat when the atomic mass is increased by a certain number or period, which between the second and third series is 16. The properties of the elements therefore repeat *periodically*. This is the foundation of the law of the *atomic mass periods*.

The first series.

The only element in the first series is Hydrogen. Its oxide formula is H_2O, its chloride formula HCl, its univalence, positiveness, etc., firmly establish it as the first member of the first series; corresponding to Lithium of the second and Sodium of the third series. The remaining six elements of the first series are undiscovered or do not exist.

Fourth series.

K, Ca, Sc, Ti, Vd, Cr, Mn, Fe, Ni, Co, Cu, Zn, Ga, As, Se, Br.

If we study the fourth series, we find that instead of seven elements, as in the second and third, we have sixteen to dispose of. The first four of these (Potassium, Calcium, Scandium and Titanium) fit perfectly into this series, in like order to Sodium, Magnesium, Aluminum and Silicon of the third series. Vanad-

ium, Chromium and Manganese are metals, while Phosphorus, Sulphur and Chlorine are non-metals; and in this respect the relationship in their case is more distant. The elements Arsenic (75) Selenium (79) and Bromine (80) are related to Phosphorus, Sulphur and Chlorine and resemble them more closely than Vanadium, Chromium and Manganese do—being non-metallic, negative, and never base-forming. It cannot be doubted that Arsenic belongs to the same group as Phosphorus; Selenium to the same group as Sulphur; Bromine to the same group as Chlorine. Arsenic is therefore given precedence over Vanadium as representative of the fifth group in the fourth series, Selenium over Chromium in the sixth group and Bromine overManganese in the seventh group. The seven principal representatives of the groups in the fourth series are therefore

E_2O, K (39); E_2O_2, Ca (40); E_2O_3, Sc, (44);
E_2O_4, Ti (48); E_2O_5, As (75); E_2O_6, Se (79)
E_2O_7, Br (80).

Between the fourth and fifth members of this series a sub-series is inserted, also arranged according to their atomic masses, their oxide formulae and other properties. The members of this sub-series are related to the principal series in a distant manner. Vanadium, with the oxide E_2O_5, represents the Phosphorus group; Chromium, with the oxide E_2O_6, represents the Sulphur group; Manganese, with the oxide E_2O_7, the Chlorine group, and Gallium, E_2O_3, the Aluminum group. These elements are evidently suited to the position given them; but Copper, which appears in the first group with the oxide formula E_2O seems to show a slight discrepancy, as it is a heavy metal and forms a higher basic oxide, E_2O_2 (CuO) and a higher chloride ($CuCl_2$). Though for these reasons Copper seems to be misplaced in the Lithium group, the arrangement is extenuated by the fact that Copper forms an oxide Cu_2O and chloride CuCl, which meet the requirements of this position; and further, this forced arrangement occurs in a sub-series.

One element is missing in the fourth group of the sub-series, representing the oxide E_2O_4. It must be a metal, because the elements in a subseries all are; it must form oxides of the general formulae of EO and EO_2; and further, its atomic mass

must be about 72, between Arsenic and Gallium. Its physical and chemical properties can also be prophesied from its position, as will appear later. The recent discovery of the element Germanium took place after its existence and physical and chemical properties had been predicted.

Three elements of this series still remain unplaced: Fe (56), Ni (59), Co (59). All the chemical and physical properties of these elements indicate classification together as one group. This eighth group is therefore inserted between the seventh and first groups of the sub-series.

Fifth series:

Rb, Sr, Yt, Zr, Nb, Mo, Rt, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I.

The fifth series is an exact counterpart of the fourth. It consists of a principal and a subseries, the elements of the former resembling those of the second and third series; while the members of the sub-series are distantly related to the second and third series. This sub-series is placed between the fourth and fifth groups, corresponding to the position occupied by the sub-series of the fourth; and to complete the resemblance, we find an eighth group of three elements between the seventh and first groups of the sub-series. These elements are included in one group (Palladium group) and have nearly the same atomic masses. They are: Ruthenium, Rhodium and Palladium.

Series like the fourth and fifth, which contain 17 elements are called *long series* or periods; while series like the second and third, which contain 7 elements, are *short periods.*

The first seven members of a long series are called an *even* series, while the last seven members are an *odd* series.

This allows of the division of the first seven groups each into two families:

Family A—the most characteristic metals in the short periods and the members of the even series of long periods.

Family B—the non-metallic or less metallic elements of the short periods, and the members of the odd series of the long periods.

Comparison between the second and third series showed

that the difference of the atomic masses of elements in the same group was 16; but that slight variations from this occurred.

If we compare the atomic masses of the third and fourth series in the same manner, we find that the difference here also is about the same. The difference between Sodium and Potassium is 16, between Magnesium and Calcium 16, between Aluminum and Scandium 17; but where subseries intervene, the principle series have a difference of from 44 to 47. Thus between Phosphorus and Arsenic, the difference is 44; between Sulphur and Selenium 47; between Chlorine and Bromine, 44.5.

The difference between the principal elements of the fourth and fifth series is from 44 to 47, conforming with the third and fourth series after the insertion of the sub-series.

This difference, approximately 46, also exists between the elements of the sub-series of the fourth and fifth series and the members of the eighth group of both series. We further find that the atomic mass of the members of the sub-series are very nearly the mathematical mean of the corresponding principal elements in the same group. For instance, the atomic mass of Copper is 63, of Potassium 39 and of Rubidium 85.

The law of the atomic mass periods therefore reads

When the elements are arranged in the order of their increasing atomic masses, the difference between the atomic masses of related elements is approximately 16; *but after the insertion of a sub-series a difference of* 44 - 47 *is observed; and further, after the insertion of a sub-series, the mathematical mean of the mass of the two elements between which it stands in the group is approximately the atomic mass of an element in a subseries.*

The sixth series.

Beside the elements previously classified, nineteen still remain, viz: Cs, Ba, La, Ce, Di, Er, Yb, Ta, W, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, Ur. It is seen that they are too numerous to be included in one series; nor are they sufficient for two complete series. The reason we have nineteen elements to dispose of now, is because we commenced a new series every time we met with an element closely related to the alkali metals: no alkali metal is known which has a greater atomic mass than Cæsium (133)—

SERIES.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VI	Group VII
	E_2O	E_2O_2	E_2O_3	E_2O_4	E_2O_5	E_2O_6	E_2O_7	
1	H 1							
2	Li 7	Be 91	Bo 11	C 12	N 14	O 16	Fl 19	
3	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5	
4	K 39 *Cu 63*	Ca 40 *Zn 65*	Sc 44 *Ga 70*	Ti 48 *Ge 72.3*	*Vd 51* As 75	*Cr 52* Se 79	*Mn 55.5* Br 80	Fe56;Ni59 Co 58
5	Rb 85 *Ag 108*	Sr 87.5 *Cd 112*	Yt 89 *In 113*	Zr 90 *Sn 118*	*Nb 94* Sb 120	*Mo 96* Te 125	? I 127	Rt 104; Rh 104;Pd 10
6	Cs 133	Ba 137	La 139 *Er 166*	Ce 142	*Di 145*			
7	*Au 196.7*	*Hg 200*	Yb 173 *Tl 204*	*Pb 207*	*Ta 182* Bi 208	*W 184*	?	Os 190;Ir 192;Pt 194
8				Th 232		*Ur 240*		

one is to be expected with an approximate atomic mass of 179 and one with a mass of 225, but no metal approaching these requirements is known with which to start the seventh and eighth series. It may be that they do not exist or that they are as yet undiscovered. However, there are sufficient reasons for placing the remaining elements in three series, so that the positions given them accord with their atomic masses, their oxide formulae and other general properties.

The arrangement of these nineteen elements is attended with much more difficulty than was met with in the preceding instances. The first difficulty arises from there being only nineteen elements to place in three series, to fill fifty-one positions. A second, that the atomic masses of these elements cannot be determined with exactness.

The sixth series, commencing with Cæsium (133), will increase until the atomic mass 179 is reached; here the seventh will begin, and increase until some alkali metal is met with having an atomic mass of about 225 (unknown). Here the eighth series commences, and will include the remainder of all known elements.

The classification of the elements in Mendeljeffs table concurs most remarkably with that according to physical and chemical properties recognised before the discovery of the periodic law. The properties of Cerium and its relatives alone can be said to be unsuited to the positions given them. The elements of the first group, Lithium, Sodium, Potassium, Rubidium and Cæsium, all resemble each other closely. Copper, Silver and Gold, though not so distinctly related to them, establish by some of their oxide formulae, valence and compounds produced (KNO_3, $AgNO_3$, etc.) their relation with the alkali metals. Isomorphous compounds of Silver and Sodium are also known.

The principal elements of the second group, Beryllium, Magnesium, Calcium, Strontium and Barium, have always been included with the alkali-earth metals previously; those which are members of the sub-group, Zinc, Cadmium and Mercury, resemble the others in their chloride (ECl_2) and oxide (EO) formulae, and the formulae of all compounds resulting from this oxide—beside many other of their compounds—are isomorphous.

The third group is also a natural one, consisting of Boron, Aluminum, Scandium, Indium, Erbium and Thallium.

The fourth group contains the elements Carbon, Silicon, Zirconium and Thorium in near relation, and, as a sub-group, Tin and Lead—all of which form a natural group; Cerium, which is also in the group, being the only objectionable addition.

The principal elements of the fifth group, Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth, have long been established as belonging to one class. The addition of the sub-group, Vanadium, Niobium and Tantalum is necessitated by the analogy of the oxide formulae, E_2O_5, and by isomorphism.

The sixth group, containing Oxygen, Sulphur, Selenium and Tellurium as principal members, and Chromium, Molybdenum, Tungsten and Uranium as more distantly related, is another very proper natural classification. The resemblance of these elements is further maintained by the fact that all the characteristic oxides are acid-forming, the acid produced having the general formula H_2EO_4 (sulphuric acid is H_2SO_4). The Potassium salts of these acids are isomorphous with those of sulphuric and selenic acids. They also resemble each other in the formation of salts which are compounds of the neutral salts with the acid-forming oxide, as

$$K_2CrO_4 + CrO_3 = K_2Cr_2O_7$$

This group is one of the strongest arguments of the accuracy of the periodic law.

The relation of the elements of the seventh group is unquestioned as far as the principal members are concerned, and the confirmation of the position of Manganese is the isomorphism of Potassium-perchlorate and Potassium-permanganate.

That the elements of the three parts of the eighth group are related, is evident from a study of their general characteristics. Nearly all the members of the group occlude Hydrogen; they form complex cyanogen compounds and complex ammonia compounds; some of them form oxides of the formula E_2O_8.

In studying the characteristics of the several different series we must distinguish between the principal and sub-series. The first element of a principal series is strongly positive and not acid-forming; as the series progresses the members gradually

change in properties until the seventh is a decidedly negative, non-basic element. The chemical contrast between the first and seventh member is always extreme. Between the seventh element of one series and th first element of the next, the chemical properties exhibit the greatest diversity, jumping from negative to positive without any gradation.

This is otherwise in the sub-series. The elements here have not such decided chemical properties. If they are acid-forming, the acids are relatively weak; if basic, not emphatically so. In fact, from the seventh group of a sub-series to the first of the next sub-series, the change is graduated by the intervening eighth group.

The gradual change in the chemical character of the elements belonging to the same group.

A gradual change of the chemical properties also accompanies the increase of the atomic mass in the principal members of each group. When the element with the smallest atomic weight is positive (like Lithium in the first group), the next (Sodium) is more positive; the third (Potassium) more than the second; the fourth (Rubidium) still more, and the last (Cæsium) the most positive of all.

In groups where the first element is decidedly negative, this negativeness decreases with the increasing atomic mass. Take for instance the seventh group. Fluorine is the most negative, Chlorine less, and Iodine the least negative.

Physical properties are also resultant from the atomic mass, as are the chemical properties.

The specific gravity, ductility, brittleness, fusibility, volatility, specific heat, conductivity, electrical status, power of refraction, etc., are all dependent upon the atomic masses of the elements.

One application of the periodic law is the prediction of the properties of undiscovered elements from the vacant places in the table. Gallium was predicted by Mendeljeff, who called it Eka-Aluminum. Lecocq de Boisbraudran afterward discovered it and named it Gallium, finding it had all the properties foretold. In like manner Scandium and Germanium were described before their discovery.

CHAPTER XVIII.

SPECTRUM ANALYSIS.

It has already been stated that white sunlight is a mixture of several colors. This can be proven by passing it through a glass prism when it forms a band of colors, the *sun-spectrum*. These colors are known as the *spectrum colors,* or *the rainbow colors.*

Seven of them are commonly recognised:

Red Orange Yellow Green Blue Indigo Violet

But as the colors gradually merge into each other, this is arbitrary; and some scientists use the following division:

1, Purple. 2, Red. 3, Orange. 4, Yellow. 5, Yellowish-Green. 6, Green. 7, Bluish-Green. 8, Blue. 9, Indigo. 10, Violet.

All ten together give white. The cause of the formation of a spectrum is that white light consists of rays of different wave-length. When passed through a prism, each ray is *differently diverted* from its direction—that is, *differently refracted.*

The angle of incidence is the angle formed by the ray of light with a line drawn *normal* to the body upon which the light acts (perpendicular to the plane of the surface).

The angle of refraction is the angle formed by the refracted ray and the normal *within* the body.

Each of the rays in sunlight has a different wave-length and different angle of refraction, causing it to produce a different sensation on the eye; the rays having the smallest angle of refraction causing the sensation of a red color, that having the greatest angle of refraction producing sensation of violet.

In fig. 21, AB is a solid wall, which has a small round hole at b, through which white sunlight, C, passes into a dark room located to the right of the wall. If the light enters the room in a straight line, a round white light-spot will be observed at d on the other side of the room. If now we introduce a glass prism into the light-rays, we see

1. That the light-spot moves away from d.

2. That the light is no longer round, but forms an elongated beam.

3. That this beam shows the rainbow colors; the purple and

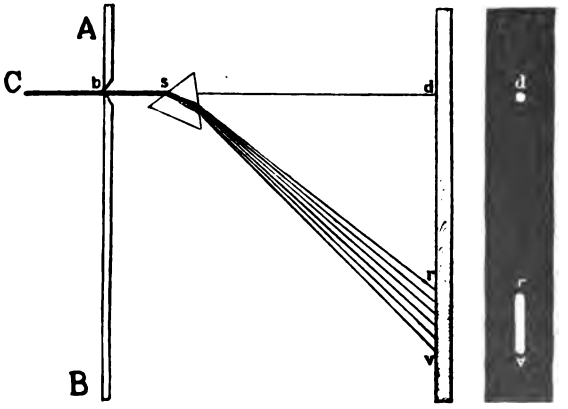


FIG. 21

red being nearest the original spot d—the purple and red rays are, then, refracted least.

Not only all ten spectrum colors result in a white light; any two of them which stand five numbers apart in the preceding list will also do so. That is, white can be formed by purple and green, red and bluish-green, orange and blue, yellow and indigo and yellowish-green and violet. These pairs are *complementary colors.*

Homogeneous or *monochromatic* light consists of light-rays of the same wavelength only. Absolutely homogeneous light

as scientifically understood, cannot be obtained by practical methods. All colors are more or less compound colors. The blue of an indigo solution is not homogeneous, for it contains some red rays. Some light is, however, practically homogeneous. The yellow light obtained when a Sodium salt is brought into a non-luminous flame is. So also is the red light obtained from common light by transmission through glass colored with sub-oxide of Copper.

The sun-spectrum contains other light-rays which do not act upon the eye, but the existence of which is proven by physical and chemical experiments. These rays lie beyond the red and beyond the violet part of the spectrum. Those portions which contain these rays are the *infra-red* and the *ultra-violet* parts of the spectrum. The infra-red are heat rays and can be detected by a very sensitive instrument for measuring temperatures. They are also called *Herschelian rays.*

The ultra-violet rays may be detected by their action upon the photographic plate, which is blackened by them. As they have this chemical action, they are called *chemical* or *actinic rays.*

A continuous spectrum is one which contains rays of every degree of refractability; and which consists therefore of a continuous band of colors which gradually merge one into another. *All solids and liquids, when heated to white heat, furnish continuous spectra.* As sunlight gives a continuous spectrum, the conclusion is drawn that the sun is a glowing solid or liquid, and not a gas.

An interrupted spectrum is produced by a light containing rays of definite wavelength and refractibility; and consists therefore of single bright lines of definite colors on a dark background. All glowing gases and vapors give interrupted spectra, as do volatile solids and liquids when heated in a non-luminous flame.

Sodium or any of its salts produce a very bright yellow line; Potassium gives a red and a violet line; Strontium gives several red lines and a blue one. These elements and their compounds also impart a distinct and characteristic color to the non-luminous flame. For instance, Sodium colors the flame

yellow; Potassium, violet; Strontium, red; Barium, green; Lithium, crimson; etc., and this coloration of the flame can be used to identify the element. When several of these elements are present at the same time, the color of one usually obscures that of the others. If Sodium and Potassium are present, the flame shows the yellow of the Sodium but no traces of the violet of Potassium. This is not so with the spectrum of such a flame. Each of the individual substances produces its own peculiar bright-colored line at a certain place, along with those pro-

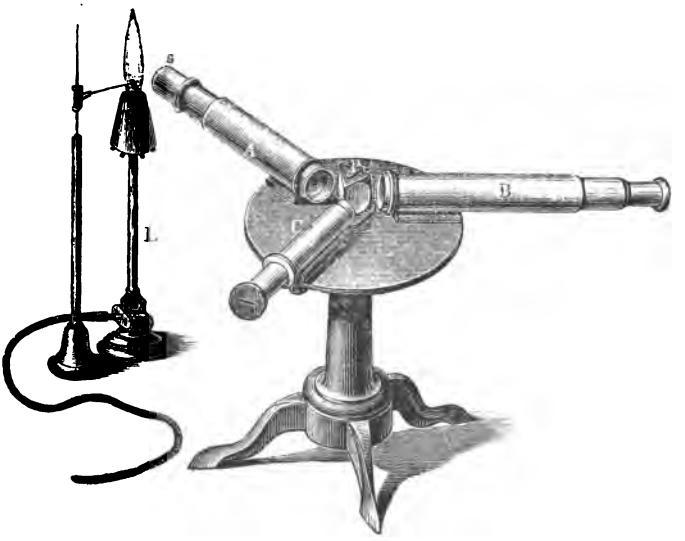


Fig. 22

duced by the other substances present. Hence it is possible to differentiate between elements by means of the spectroscope.

Spectrum analysis is a process of investigating substances by examining their spectra. It was practised in 1859 by Kirchhoff and Bunsen and they deserve credit for one of the most important discoveries of mankind.

In order to conveniently conduct spectrum analysis, a *spectroscope* is used (fig. 22). This comprises a table-like support,

in the body of which is placed a glass prism, P. The tube A has a vertical slit at its end, through which the light to be examined enters the tube. This is then directed upon the prism by a collecting lens, placed in the interior of the tube. The spectrum formed is observed by the telescope B. The tube C has a horizontal slit at its end, here a millimeter-scale, engraved in glass, is fastened. A luminous flame placed before this slit throws the image of the scale upon the surface of the prism, which reflects it into the telescope B. In looking into B. the spectrum of the flame and the millimeter scale are both seen at the same time; the relative position of the lines in the spectrum can thus be easily determined.

In spectrum analysis we recognise

EMISSION SPECTRA AND ABSORPTION SPECTRA.

Emission spectra.

In order to produce an emission spectrum, the substance to be examined is heated to white heat and thus vaporised, at a place not far away from the slit of tube A. The vapors glow, and the spectrum may be observed through the telescope B. Therefore

Emission spectrum is a gas spectrum; that is, an interrupted *spectrum consisting of bright lines of definite color and position.*

If a solid is to be examined, a portion is placed in the loop of a Platinum wire and heated in a non-luminous bunsen-flame. Many metals, however, are not volatile in such a flame. In order to vaporise them, wires composed of the metal are used as electrodes and an electric spark passed between them. Traces of them are thus vaporised.

Another method is to place a solution of a salt of the metal in front of the slit in tube A, and put the negative pole of a battery in the solution; the positive pole being held just above the surface of the solution. When electric sparks pass between the surface of the liquid and this latter pole, some of the metallic salt in solution will vaporise, and emit a spectrum.

In order to observe the emission spectra of gases, they are enclosed in a rarified condition in *Geissler's tubes.* Through the walls of these tubes small Platinum wires are melted, and these

serve as the poles of an induction apparatus. If sparks are passed through these tubes, the gas commences to glow and gives its characteristic spectrum. Hydrogen glows with a red light, and Nitrogen with a violet light. If one of these glowing gases be held before the slit in tube A, the spectrum it forms can be examined. The Hydrogen spectrum is seen to consist of a red, a blue and a green line; the Nitrogen of a great number, mostly in the violet, etc.

Absorption spectra.

Before this form of spectrum can be understood, absorption of light must be explained.

Bodies are either opaque or transparent. *A transparent body* is one that offers no resistance to the passage of light (glass). *An opaque body* offers resistance to the passage of light. The light which acts upon an opaque body is either reflected or, penetrating into the body, is converted into other kinds of energy (heat, chemical energy). This is the *extinction* or *absorption of light.*

Photo-thermal absorption occurs when light entering a body is converted into heat.

Photo-chemical absorption is the conversion of the light entering a body into chemical energy.

Some transparent bodies transmit all kinds of light-rays practically unabsorbed; such transparent bodies are therefore white or—as they are usually called—colorless(window-glass); but not all bodies do this. Some are transparent to certain rays, while others of a different wavelength are absorbed. The rays not absorbed determine the color of the light after passing through the body. A monochromatic or a mixed color will be produced according to the rays that pass through.

Use is made of this fact in analytical chemistry. Sodium imparts a yellow color to the flame, Potassium a violet one; but the intensity of the Sodium flame is so much greater than that of the Potassium, that the violet color of the latter cannot be noticed when both are present—the flame is yellow. If this is viewed through a Cobalt-colored glass, however, the violet of the Potassium can be discerned, while the yellow of the Sodium

cannot be seen; the Cobalt glass is opaque to the rays of the Sodium spectrum.

Bodies (solids, liquids and gases) which are colored and transparent in sunlight possesses these properties only because sunlight contains rays of all possible refractibility, and therefore some which are able to pass through each of these bodies.

If such a color-transparent body is subjected to rays of another wavelength which are absorbed, the body will appear black (it is therefore opaque). If light which gives a continuous spectrum is passed through such a body, the spectrum, although still a continuous one, will show lines or bands corresponding to those rays which have been absorbed. It follows

An absorption spectrum is a continuous one having black lines which interrupt the merging of one color into another. It is obtained by placing a light giving a continuous spectrum (sunlight, Calcium light, oil lamp, luminous gas flame, etc.) before the slit of tube A of the spectroscope. The transparent body to be examined is then placed between the slit and the light, and the spectrum observed. The position of these *absorption bands* is characteristic.

If the absorption spectrum of a liquid is to be examined, it is placed in a square-shaped glass vessel—an *absorption cell*—between the slit of the spectroscope and the light.

The absorption spectra of elementary gases are important. The position of the black bands in their absorption spectra are identical with the position of the colored bands of their emission spectra. If a white light is examined after passing through glowing Sodium vapors, a distinct black band, at the same place where the emission spectrum of Sodium shows a yellow band, will be seen. Such spectra are *inverted spectra,* because the portion that shows black in the one shows colored in the other and vice versa: hence

When light is passed through glowing gases, they absorb those light-rays which they emit.

The sun is a glowing solid or liquid, emitting an intense light, surrounded by an atmosphere of glowing gases—Sodium vapors,

Potassium vapors, etc. The light emitted would produce a continuous spectrum were there no intermediate agent; but we know that it passes through an atmosphere of glowing gases because the spectrum contains dark lines. These are the *Fraunhofer's lines,* and from their position we can deduce the elements of the sun's atmosphere.

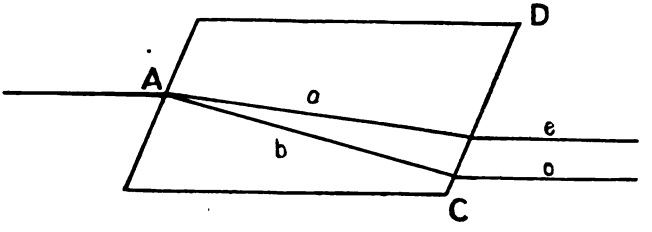


Fig. 23

Spectrum analysis is exceedingly accurate. It is possible to detect one three-millionth of a milligram of Sodium with certainty by its aid. Several elements, as Cæsium, Rubidium, Thallium, Indium were discovered by spectrum analysis.

CHAPTER XIX.

THE POLARISCOPE.

If a spot of ink be made upon a sheet of paper and a transparent glass plate laid on it, we can distinctly see the inkspot on the paper; if we revolve the glass plate, the inkspot is evident at

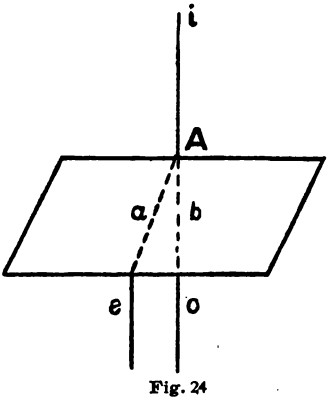


Fig. 24

all times. But if a crystal of calcite (natural crystallised Calcium-carbonate) is laid upon the inkspot in the place of the glass, the results are quite different. Now we see two spots, which are of equal definition. If we look through a calcite crystal towards a light, two images of the light are seen. This phenomenon is *double refraction.* Not only calcite crystals but many others will do this. The explanation is as follows.

When a ray of light falls upon a calcite crystal, it is here split into two separate rays, a and b (fig. 23). Both of these

possess different angles of refraction. The velocity of the ray i A in the crystal is retarded more in the direction b than in the direction a; and the ray b is diverted more from the original direction of the ray than is a. The distance which the ray a travels in the crystal is therefore greater than that traveled by b (a longer than b). b is called the *ordinary ray,* while a is the *extraordinary ray.*

At the opposite surface, CD, of the crystal, both rays pass out; the ordinary ray as o, the extraordinary as e. Both are parallel and of equal intensity. If the original ray of light reach the surface of the crystal as normal (perpendicular to the plane surface, fig. 24), it likewise splits into two rays. The ordinary ray, possessing the lesser velocity, will follow the shortest way, b, through the crystal and pass out as o; the extraordinary, having the greater velocity, will take a longer way, a, and pass out as e. The rays o and e are parallel and of equal intensity.

Suppose that i is an inkspot on paper, and that the calcite crystal is placed on this while the eye of the observer meets the rays e and o, two spots of equal brightness will be seen. If we now revolve the crystal on the paper, the ordinary spot remains in the same place, while the extraordinary revolves around it. It is to be expected that if we repeat the experiment with one of the two refracted rays by allowing it to pass through a second calcite crystal, that it will again divide into two rays of equal brightness; but this is not the case. It splits again into two rays, but these are not of equal brightness—except when the crystal is turned to a certain position.

Suppose that the original ray, iA, (fig. 25), enters the first calcite crystal at the point A; it is split into two rays, the ordinary, b,-o, and the extraordinary, a,-e. Now remove one of these, say the extraordinary, by means of a piece of opaque cardboard, C, and then permit the second ray, o, to enter a second crystal, II. The ray o is again split into two, the ordinary, b_1, and the extraordinary, a_1; but these are not of the same brightness in all positions of the crystals. If we revolve the calcite crystal II, we observe that one of the images, e_1 or o_1, increases in brightness, while the other decreases; and when one has attained its maximum brightness ,the other is dark and

cannot be seen. On further revolution, the bright one will gradually become darker and finally disappear; while the other becomes bright in the same ratio, until it is brightest at the time the other is completely dark. The two images appear and disappear alternately.

In order to decrease the light of either from the maximum to the minimum or vice versa, it is necesary to go through an arc of 90°. This experiment proves that the ray of light i acts in a different way on the calcite crystal I than does the ray

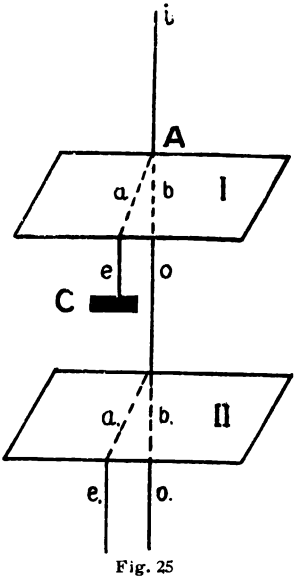


Fig. 25

o on the crystal II; the properties of o and i are not identical. The ray o is a *polarised ray* in contradistinction to the *common* light-ray i. The cause of this difference is that the common ray is doubly refracted by passing through the calcite plate —the ordinary and the extraordinary rays when they pass out possess the same brightness, even though the calcite crystal be revolved; while the polarised ray is also doubly refracted by passing through the crystal, but here the ordinary and the extra-

ordinary rays which pass out alternate from darkness to brightness and vice versa when the calcite crystal is revolved.

The calcite crystal I, which changes the common light-ray into two rays of polarised light is the *polariser;* calcite crystal II, which by its revolution causes the alternation of light and darkness, and distinguishes between the polarised and common light, is the *analyser.*

Nicol's Prism.

It is inconvenient to have two rays formed when the light passes through the calcite crystals, and is is advisable to elim-

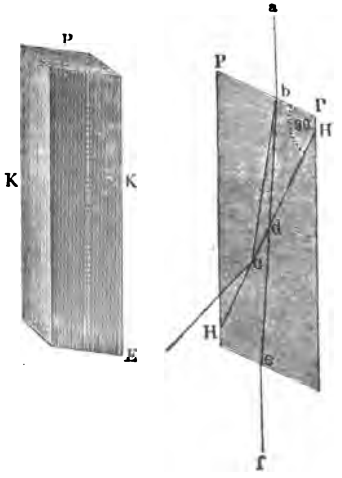


Fig. 26 — a, b.

inate one. It matters not whether we remove the ordinary or the extraordinary, as both are polarised. This is done by means of a *Nicol's prism.* The construction of this prism is based upon the principle of *total reflection.*

If a ray of light enters from a rarified medium into a denser one, the angle of refraction is smaller than the angle of incidence; and vice versa, if a ray of light passes from a dense into a more rarified medium, the angle of refraction is greater than the angle of incidence. Suppose a ray of light travelling in glass reaches the border of the glass in a very oblique manner,

the angle of refraction will be still larger, the ray cannot pass from the glass at all but is *totally reflected* and travels back into the glass.

A long calcite crystal (fig.26 a) has end faces P which naturally form angles of 71° with the long vertical edges K. These end faces are cut in polishing so that the angle mentioned is changed to 68°. The crystal is then cut diagonally by the line HH (fig.26 b), which is laid so that it forms right-angles with the polished faces. The two surfaces of the sections obtained are well polished and cemented together again by Canada balsam. Fig. 26 b shows a cutting through a Nicol's prism.

If a common ray of light, a-b, coming from the air enters the prism at b, it is split into two rays, the ordinary, b-c, and the extraordinary, b-d—both traveling in a dense medium, the crystal, until they reach the less dense layer of Canada balsam, HH. Here the ordinary ray, b-c, reaching the balsam-layer in a very oblique direction, is totally reflected sideward; the extraordinary ray, reaching the balsam in a less oblique direction, passes through it into the second part of the calcite block in the direction of d-e and enters as e-f into the air. Hence, if the eye of the observer is placed near f, only the extraordinary ray will be seen. In other words, one image results.

An arrangement of two Nichol's in this manner is a *simple polarisation apparatus.*

If one of the Nicol's is revolved, the image will alternately appear and disappear; the magnitude of the revolution being 90° from the point of maximum brightness to the point of maximum darkness. and vice versa.

Tourmaline, cut into thin plates, is also a good polariser.

A ray of common light can be polarised by reflection as well as by refraction. If a ray of common light falls upon a blackened and polished glass surface with an angle of incidence of 54°35, polarisation is effected. For details of the various methods the student is referred to text-books on physics.

Action of polarised light on solutions of organic substances.

Many organic substances (those which contain Carbon and are the product of an organism) have the property of rotating polarised light. This is determined as follows;

The prisms of a polariser are so rotated that light is entirely invisible through the instrument. A glas containing a solution of sugar is placed between the two prisms; the polarised light, traveling from the first to the second prism, must pass through this. If we now look through the analysing Nicol, we are able to see the light; and, in order to make the field dark, it is necessary to turn the prism to the left a certain number of degrees. Hence the sugar solution has rotated the plane of the polarised light to the right, because after its passage through the sugar solution it does not fall upon the second prism in the same manner as before. The analysing Nicol must be turned the other way (to the left) to restore the initial state.

Circular polarisation is the rotation of the plane of polarised light.

Optically active substances rotate the plane of polarised light to the left or to the right. They are divided into two classes

(a). *Dextro-rotary* or *dextro-gyrate bodies*—those which rotate the plane of polarised light to the right.

(b). *Laevo-rotary* or *laevo-gyrate*—those which reflect the plane of polarised light to the left.

Optically inactive substances do not rotate the plane of polarised light.

The angle of rotation is that through which the plane of light is rotated.

For the purpose of measuring the angle of rotation exactly, one of the Nicol's of a polariser is fastened firmly, while the other (usually the analyser) is set in a tube which can be rotated around its own axis and which, when rotated, moves an indicator over a scale. Rotation-angle is usually designated by the letter a.

The laws of the circular polarisation of liquids and solutions:

1. *The rotation-angle is directly proportional to the thickness of the liquid layer through which the polarised light passes.*

To compare optical rotation, it is then necessary to have a standard of thickness; this is 10 centimeters. Every polarisation

apparatus is fitted with tubes of one and two decimeters and sometimes with tubes of four and six decimeters. In use, the ends of these tubes are closed by glass plates, so that the polarised light is able to pass through the whole length of the tube.

2. *Temperature influences the rotation-angle, the latter decreasing with increasing temperature.* Hence a standard temperature (15°) is recognised.

3. *The color of the light passing through the apparatus influences the rotation-angle.* For instance, the rotation-angle of bodies examined in violet light is far greater than if examined in red light. Homogeneous or monochromatic light of a yellow color is selected as standard. It is produced by placing a bead of Sodium-chloride on a Platinum wire in a non-luminous flame.

4. If the substance to be examined is a solution of an optically active body in an optically inactive solvent, *the rotation-angle is proportional to the concentration.* It is therefore necessary to adopt a certain concentration as standard. The standard adopted is 100; that is, all rotation-angles should be computed to concentration of the solution equal to 100 grams of the active substance in 100cc. of the solution.

When all the conditions (1 - 4) are observed, we obtain the specific rotation-angle.

The specific rotation-angle is that produced by a solution of 100 *grams of the optically active substance in* 100 *cc. of the solution when enclosed in tubes of one decimeter length and examined by Sodium light at a temperature of* 15° C.

It is usually designated [a]D.

As not all these conditions are practicable, the specific rotary angle is computed from the ordinary rotation-angle (a) as follows:

Let l equal the length of tube in decimeters; c the concentration—that is, the number of grams of active substance in 100 *cc.* of the solution; p the percentage—the number of grams of active substance in 100 *grams* of the solution; a, the observed rotary-angle; d, the specific gravity of the solution.

As a layer of l decimeters produces a rotation angle of a°, a layer of one decimeter produces a rotation angle of a:l .

Suppose the solution has a concentration of c grams in 100 cc. If it had a concentration of 1 gram in 100 cc., the rotation-angle would be a:l.c and when the concentration is 100 grams in 100 cc. it will be (a.100 : l.c)°. Hence

$$[a]D = \frac{100a}{l.c}$$

Assuming that the solution has a specific gravity of d, then 100 cc. of the solution weigh 100d, and contain c grams of the active substance. Hence 100 grams of the solution contains c:d grams of the active substance, and

$$p = \frac{c}{d} \text{ or } c = d.p$$

If this value of c is placed in the above equation, we obtain

$$[a]D = \frac{100a}{l.d.p}$$

Circular polarisation caused by minerals.

Suppose that, using white sunlight, we place the two Nicol's of a polarscope so that the field is dark, and then place between the two a plate of quartz cut perpendicular to the principal axis of its crystal; the field is now seen to be colored. If we rotate the analysing Nicol, the color changes—it does not do so when the quartz plate is rotated. The explanation of this phenomenon is that the quartz crystal is optically active, and rotates the polarised light, the field of vision which was previously dark becoming light. The quartz plate rotates the planes of the various colored polarised rays differently. It rotates polarised red rays in a far lesser degree than violet rays—the rotation-angle of red light being smaller than that of violet light.

As white sunlight is composed of different colors, it is evident that the field of the polariscope must appear colored and

that the colors change as the analyser is rotated. If different quartz plates are examined, it is found that some rotate the polarised light to the right, others to the left; the rotation-angle being always of the same magnitude in plates of equal thickness. If we examine the crystal, we find that in both cases they consist of six-sided, prismatic pyramids, of which certain corners are truncated and replaced by faces. Quartzes which are dextro-gyrate have the truncation faces in a position the reverse of that they occupy in laevo-gyrate quartzes. The real image of

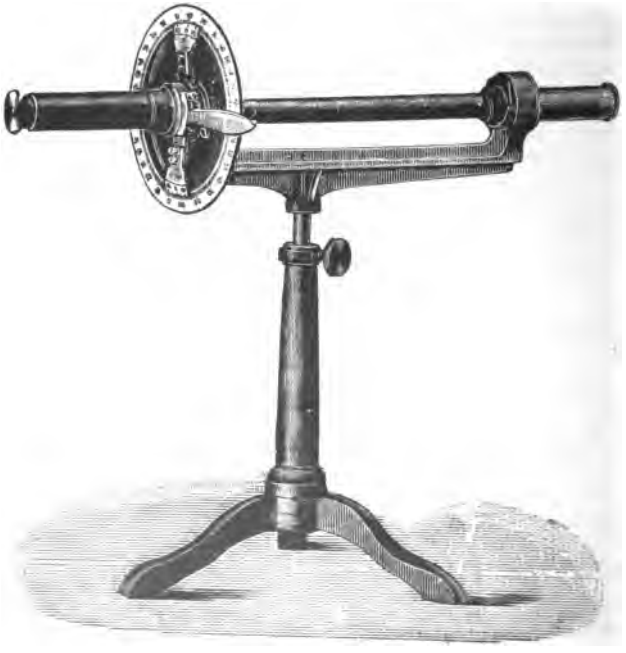


Fig. 27

a dextro-gyrate quartz being the same as a mirror image of a laevo-gyrate quartz.

The nature of circular polarisation depends upon the crystalline form.

POLARISCOPES.

A polariscope is an apparatus used to determine the action of polarised light upon bodies. There are a great many varieties of polariscopes of varying description; here we will give only the principles of those most used in chemical work.

They usually consist of two Nicol's, the polariser and the analyser, fastened in the two ends of a brass tube in such a manner that one of them can be rotated in this tube (fig.27). The part of the brass tube between the prisms can be opened and a glass tube containing the liquid to be examined can be inserted

This form has the disadvantage that it is difficult to determine the point of maximum darkness and maximum brightness of the field. Upon rotating the prism, the field remains dark during several degrees. In order to fix the zero point more exactly, secondary attachments are added; according to the construction of these adjuncts, polariscopes may be divided into

1. Those to be used with white sunlight.
2. Those to be used with monochromatic yellow light.

1. *Polariscopes to be used with white light.*

The principal apparatus of this kind is that of Soleil-Scheibler. This is characterised by a double quartz plate. Two quartz plates, both of a thickness of 3.75mm. are cut off from quartz crystals; one from a dextro-gyrate crystal, the other from a laevo-gyrate crystal. The edges of the two are approximated, forming a double plate. This is then placed between the Nicol's so that the section line between the two is vertical, and divides the field of vision into two parts. As one of the halves of the quartz plate is laevo-gyrate while the other is dextro-gyrate, both sections of the field of vision will appear in different colors; when one half appears violet, the other appears red. When rotating the analyser, the colors alternate from red to violet and back to red again in each section. There will occur a place during the rotation of the analyser (between violet and red) at which both halves show the same color—that is, purple. This purple coloration is the *couleur sensible* and can be definitely noted. This position is the zero point.

2. *Polariscopes to be used with homogeneous yellow light.*

There are two principal divisions of this class:

(a). *Half-shadow apparatus.*
(b). *Interference apparatus.*

(a). *Laurent's half-shadow apparatus.* The light used is produced by placing a piece of Sodium-chloride in the loop of a Platinum wire in a non-luminous flame. It is advisable to use lamps specially constructed for this purpose. A plate, cut from a crystal of red Potassium-bichromate is fastened before the polariser of a Laurent's apparatus; this is intended to prevent traces of light, other than yellow or red, from entering the apparatus.

The characteristic attachment of a Laurent's apparatus is a circular glass diaphragm, half-covered by a quartz plate which is affixed to it. This diaphragm is placed between the polariser and the analyser so that a semi-circle of quartz and one of glass are in the field of vision.

If we look through such an apparatus toward a yellow Sodium light, we will observe a round field which is divided diametrically by a vertical line into two semi-circles. If one of the prisms is rotated, one of the semi-circles is seen to become darker, the other lighter alternately. The intensity of both become equal at a certain point, the *zero-point.*

This phenomenon is caused by the fact that the semi-circle of glass does not rotate the plane of polarised light, while the quartz does; and it is evident that when the glass portion shows its maximum light intensity that portion covered by the quartz plate will be darker.

(b). *Wild's polaristrobometer.* Looking through this apparatus toward a yellow light, a round field with a cross-thread of and a number of dark horizontal stripes (interference stripes) are observed. If one of the Nicol's is rotated, the stripes will disappear until the field is finally free of them. This is the zero point of the graduation. If the prism makes one complete circular rotation, the stripes disappear four times; therefore the positions where no stripes can be seen lie 90° apart. The peculiar attachment of the Wild's apparatus, which produces the inter-

ference stripes, is the *Savart plate.* It consits of two calcite plates cut from a crystal in such a manner that the surface of the plates form an angle of 45° with the optical axis of the crystal. The two plates are cemented together in crossed position. The theory is as follows:

Light is a wavemotion. If two light-rays of different wave-length travel the same road, increased darkness as well as increased light will be produced along their path. Darkness will be produced when the wave-crest of the one coincides with the wavetrough of the other. This is *interference of light.*

In the Wild's apparatus, the common light-ray is first polarised by one of the Nicol's. The polarised ray enters the Savart calcite plate; but as calcite is a mineral having double-refraction, it is resolved into two components within the plate, the ordinary and the extraordinary, which diverge at right angles to each other and travel with different velocities and different wave-lengths. In the second Nicol's each of these component rays is again split into two, and those of the last division which move in the polarising plane are transmitted and produce interference phenomena. These are seen as colored stripes if the light used is white, or black if monochromatic light is employed.

In addition to the parts mentioned, polariscopes contain lenses so arranged as to magnify the image.

Part II

SPECIAL CHEMISTRY

OXYGEN.

SYMBOL, O; AT. MASS, 16; VALENCE, II.

Physical properties:

It is a colorless, odorless, tasteless gas, a little heavier than air. It is only slightly soluble in water, but sufficiently so to support the life of fish. When compressed and chilled to a very low temperature, it liquifies and forms a steel-blue, mobile liquid which boils at —181° C.

Occurrence:

Oxygen occurs the most frequently of all elements. Nearly one-half of the earth's crust (by weight) is Oxygen. It is also found

1. In the air, which is a mixture of about 79 percent of Nitrogen and 21 percent of Oxygen, and some few other constituents of lesser importance.

2. In water, which is a compound of 8 parts O and 1 part H (by weight).

3. In chemical combination in organic products, the living animal and plant containing about 80 percent of it.

4. In many minerals, in combination with other elements.

Chemical properties:

Oxygen does not burn, but other bodies burn in it with increased light and heat. If a piece of wood on which there is but a glowing spark be introduced into a bottle of Oxygen, it immediately bursts into bright flame. Phosphorus burns in it with such an intense light that it is painful to the eye to watch the process. Sulphur burns in Oxygen with a blue flame.

When a substance unites with Oxygen, it forms an *oxide*. The process is that of *oxidation*. An oxide can burn no more if completely saturated with Oxygen.

If a compound burns in Oxygen, the elements burn separately and an oxide of each is formed. When Hydrogen-sulphide burns, it forms oxide of Sulphur and oxide of Hydrogen. If wood, which is a compound of Carbon, Oxygen and Hydrogen, burns, it forms oxide of Hydrogen and oxide of Carbon, the Oxygen of the wood helping that of the air to complete the process. The fixed impurities of the wood remain as ash.

There are two kinds of oxidation processes:

1. *Combustion*—the process of combining a substance with Oxygen, accompanied by the production of light and heat. The weight of the products of combustion is equal to the weight of the burned substances plus the amount of Oxygen taken up. The common materials used for burning are wood, coal, and oil; and when they are burned, the products are Carbon-dioxide (CO_2) and water (H_2O), which at that temperature are both gases and consequently escape. Therefore it is not directly evident that the weight of the product is equal to the factors of the reaction, but it is, nevertheless, substantiated experimentally.

Supporters of combustion are gases in which other bodies can burn. Oxygen is a supporter of combustion.

2. *Spontaneous oxidation*—a slow oxidation without observable light and heat, as the rusting of iron.

Oxidation can be brought about in two ways:

(a). *Direct oxidation,* using the free Oxygen of the air.

(b). *Indirect oxidation,* treating the substance to be oxidised with some easily-decomposible compound rich in Oxygen. Such compounds are *oxidising agents*; all substances having the prefix 'per' (as permanganate of Potassium), nitric acid, Chlorine-water, chromic acid, Potassium-chromate, are oxidising agents. Indirect oxidation is more powerful than direct. Iron oxidises or rusts very slowly in air, but can be oxidised in a short time by means of oxidising agents.

The reverse process—that is, when Oxygen is taken away from

compounds, is *reduction* or *des-oxidation*; and substances which will bring this about are *reducing agents*. Examples of reduction are the heating of a substance with coal, a process much used in the reduction of ores; the heating of a substance in a stream of Hydrogen, as in the reduction of Iron-oxide, where a fine Iron-powder is obtained. All compounds having the prefix 'hypo' or the affix 'ous' or 'ite' are reducing agents.

Many bodies, in burning, first change into gas and then burn with flames. Hence a flame is a burning gas. These gases which produce the flame are formed by evaporation (when alcohol, gasolene, etc. burn) or by chemical decomposition (when wood, coal, candles, etc. burn).

There are two kinds of flame: luminous (as gas light) and non-luminous (as an alcohol light). If a porcelain dish be held in a gas flame, a black coat is seen to form on the dish—this is composed of solid particles which were suspended in the flame, where, heated, they glow and give forth light. This introduction of a solid into the flame is the most important cause of luminosity. Ordinarily it is coal particles that are suspended, for the common burning materials are composed of Carbon, Hydrogen and sometimes Oxygen. There is not usually sufficient Oxygen present in air to burn all the elements of the compound at once, so the Hydrogen, being more readily ignited, burns and particles of Carbon are separated into the flame, where they glow and give heat. This is *incomplete combustion.*

Hence an alcohol flame can be made luminous by bringing it into an atmosphere containing less Oxygen, or by dissolving substances rich in Carbon in the alcohol.

Drummond's calcium light is a non-luminous, Oxy-Hydrogen flame made luminous by the introduction of a piece of lime. Auer von Welsbach has brought forward an invention based on the same principle. It is a non-luminous flame, on which is placed a mantle made of the oxides of metals which glow and give a bright light.

The Bunsen burner gives a non-luminous flame. There are holes at the bottom of the burner through which air is drawn in, conducting sufficient Oxygen to the flame for complete combustion. If these are closed, the flame becomes luminous.

A common luminous flame has three parts:

(a). A non-luminous interior, where the fuel changes into gas.

(b). A bright part surrounding this wherein the Hydrogen burns and the coal particles glow.

(c). A non-luminous margin where all the fuel burns.

The oxidation-flame is produced by putting the tip of a blow-pipe into the outside, non-luminous part, and blowing hard.

The reduction-flame is produced by blowing gently, with the tip in the luminous part.

The ignition temperature is that to which a body must be heated in order to start it to burn; and

Combustion temperature is that produced by the burning.

The combustion temperature is higher than the ignition temperature. If this were not so, the body would not continue to burn, as the portion not yet lit would not be heated to the ignition temperature by the contiguous, burning portion.

When a flame is cooled sufficiently to reduce its temperature to below the degree necessary for ignition of the body, burning ceases. This occurs in blowing out a light. A gentle draught increases the rapidity of combustion, as an excess of Oxygen enters the flame without it being cooled below the ignition temperature.

Respiration is a process of oxidation in animals whereby air is taken into the lungs, and a part (4 to 5 percent) of the Oxygen retained and passed into the blood. The peculiar substance which has the power thus to take up Oxygen is the *haemoglobin* contained in the red blood corpuscles. This spontaneously oxidises and forms *oxy-haemoglobin,* a bright red substance to which the red color of arterial blood is due. Oxy-haemoglobin is a compound in which the Oxygen is but very loosely bound and easily breaks up into free Oxygen and haemoglobin. Thus with the circulation of the blood a stream of Oxygen is carried to all parts of the body and performs oxidation processes with the elements of which the body is composed. This chemical action furnishes the necessary energy for the work of the various organs, just as the combustion of the coal under a boiler supplies the energy which drives the engine.

Animal life is a process of oxidation, while *plant life* is largely a process of reduction. As animal tissues consist of compounds of Carbon, Oxygen, Hydrogen, Nitrogen, Sulphur and Phosphorus, oxides of these elements are formed in animal metabolism. The Hydrogen forms water (H_2O); the Carbon Carbon-dioxide (CO_2), which, being a gas, is exhaled; the Sulphur forms Sulphur-trioxide (SO_3), which, with water, yields

Fig. 28

sulphuric acid (H_2SO_4) and this with the alkalies of the blood forms soluble sulphates which are passed out in the urine; the Phosphorus forms phosphoric-oxide (P_2O_5) and this with water phosphoric acid, which, uniting with the metallic elements of the blood, forms phosphates (these are also passed out through the urine); the Nitrogen is oxidised to various compounds, the

principal of which are urea, uric acid and the purine bases, finally passed out in the urine.

By the process of exhalation, the constituents of the air not consumed (the Nitrogen, the Oxygen not used, etc.), together with the gases formed by the oxidation of the tissues (Carbon-dioxide, etc.) are given up.

Preparation of Oxygen.

1. *By electrolysis*—passing an electric current through water—whereby it is split into Oxygen and Hydrogen; the Oxygen being formed at the positive pole, the Hydrogen at the negative. Then Oxygen is an electro-negative element, Hydrogen an electro-positive one. The volume of the latter is just twice that of the former.

$$H_2O = 2H + O$$

A convenient apparatus for electrolysis is shown in fig. 29.

2. By heating Mercuric-oxide, which splits into Mercury and Oxygen:

$$HgO = Hg + O$$

3. By heating black oxide of Manganese, when Oxygen and a lower oxide of Manganese is formed:

$$3MnO_2 = Mn_3O_4 + 2O$$

4. By heating black oxide of Manganese with sulphuric acid. Manganous-sulphate and water are formed and Oxygen freed:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$

5. By heating Potassium-chlorate, which forms Potassium-chloride and free Oxygen:

$$KClO_3 = KCl + 3O$$

It is convenient to mix the Potassium-chlorate with some black oxide of Manganese. Then the generation of Oxygen takes place very evenly without melting or foaming and at a far lower temperature. The Manganese-dioxide acts as a katalyser and is unchanged at the end of the reaction.

6. Other processes for the preparaton of Oxygen are: heating a mixture of Potassium-permanganate and sulphuric acid; heating a mixture of Potassium-dichromate and sulphuric acid; heating dry Barium-dioxide (BaO_2), which splits into Barium-oxide (BaO) and O; treating Hydrogen-dioxide with Potassium-permanganate, etc.

History:

Oxygen was discovered independently by Priestley in England (1774) and by Scheele in Sweden (1775); but the great importance of Oxygen in combustion and oxidation was shown by Lavoisier of France, who propounded the modern theory of combustion (1775-1781).

OZONE (O_3).

Ozone is an allotropic form of Oxygen, its molecules consisting of three atoms of Oxygen; while the atom of the ordinary Oxygen has but two atoms. It is a colorless gas of a peculiar odor which is suggestive of Chlorine or Phosphorus. In diluted condition, its smell is refreshing, but is very irritating when concentrated. It is one and a half times as heavy as Oxygen, and is formed when silent electric discharges act on dry Oxygen or air. This may be brought about by the *Siemens ozone tube,* which consists of two glass tubes, one inside the other. There is a space between the tubes. The external wall of the outer tube and the internal wall of the inner are coated with goldleaf, which forms the poles of an induction apparatus. Oxygen is then passed through the space, and a portion of it (5 to 6 percent) is converted into ozone.

Ozone is contained in the air after a thunderstorm, and causes a refreshing feeling. It is also formed by some essential oils, as turpentine, on exposure to air. It sometimes causes the corks of bottles containing these oils to become bleached.

Ozone is also formed

(a). During many processes of slow oxidation. If small pieces of Phosphorus are put into a bottle, half-covered with water, and allowed to stand for a few hours, the air in the bottle is ozonised.

(b). During many processes where Oxygen is liberated. For

instance, when small portions of Potassium-permanganate or Barium-dioxide are added to sulphuric acid.

Ozone can be liquified by cooling, forming a dark-blue liquid. It is more easily condensed than Oxygen. It is a strong oxidising, bleaching and disinfecting agent. It liberates Iodine from Potassium-iodide. It may be detected by dipping a piece of white filter paper in a solution of starch and Potassium-iodide and then bringing this paper into the solution to be tested. If ozone is present, the paper will turn blue.

Organic substances are oxidised very energetically by ozone, and all rubber connections must be avoided in the apparatus used for its preparation.

History:

Ozone was discovered by Schoenbein in 1840

HYDROGEN.

SYMBOL, H; AT. MASS, 1; VALENCE, I.

Occurrence:

Hydrogen is rarely found in the free state on our earth (only in the gases of volcanoes), but in large quantities on the sun and other heavenly bodies which are in an earlier stage of evolution. In chemical compounds we meet with it very frequently. It is contained in water, which is a compound of 8 parts of Oxygen and 1 part of Hydrogen (by weight). It is also contained in combined state in all animal and vegetable products.

Physical properties:

It is a colorless, odorless and tasteless gas, insoluble in water; it can be liquified only by great pressure and at very low temperature—it is much harder to liquify than Oxygen. It is the lightest of all known substances, being about 0.07 times as heavy as air. It is used in balloons. Hydrogen penetrates porous bodies easily, and diffuses therefore through membranes. It also penetrates heated solid metals (see occlusion).

It burns with a bluish non-luminous flame, forming water. The Hydrogen flame is exceedingly hot and can be intensified by blowing Oxygen into it. This is known as the *Oxy-Hydrogen flame.* A burner, consisting of a tube through which Hydrogen passes from a tank, and of a second tube leading Oxygen to the escaping Hydrogen, is called an *Oxy-Hydrogen burner.* This will produce one of the highest temperatures attainable by chemical action. Even Platinum melts in it. It is much used in various industries and arts. In order to make the Hydrogen flame luminous, it is necessary to place a solid in it, or to charge the gas with some volatile substance containing much Carbon. A mixture of Oxygen and Hydrogen in the proportion of two volumes of the latter to one of the former is an *Oxy-Hydrogen* or *detonating mixture.* It is extremely explosive when heated. Hydrogen also explodes when mixed with air. and ignited. We must therefore be very careful in experiments with Hydrogen, and before igniting it see that no air is present. It may be ignited not only by fire, but also by the electric spark or by contact with Platinum black (see katalysis).

Preparation:

1. By the electrolysis of water.

$$H_2O = 2H + O$$

2. By passing watersteam through heated Iron pipes—the Iron withdraws the Oxygen, forming Iron-oxide, and frees the Hydrogen:

$$4H_2O + 3\ Fe = Fe_3O_4 + 8H$$

3 By heating a mixture of slaked lime and Iron. The Iron decomposes the water contained in the slaked lime in the same manner as in 2.

4. By a similar method to 2, using Carbon instead of Iron:

$$H_2O + C = CO + 2H$$

When made in this way, the Hydrogen contains Carbon-monoxide gas; but as this is also combustible, it may be used for burning.

5. Hydrogen can be produced by passing watersteam over

heated metallic Magnesium, forming Magnesium-oxide and Hydrogen:

$$Mg + H_2O = MgO + 2H$$

6. By boiling water with a Zinc-Copper couple (metallic Zinc which has been thinly coated with metallic Copper). Zinc-oxide and Hydrogen are formed:

$$Zn + H_2O = ZnO + 2H$$

7. By treating certain metals, such as Zinc or Iron, with a diluted acid. Free Hydrogen and a salt of the metal are formed:

$$Zn + H_2SO_4 = ZnSO_4 + 2H$$

This is the most convenient method in chemical laboratories.

8. By boiling certain metals (Zinc, Aluminum, Iron, Magnesium) with water and an alkali hydrate. Hydrogen and a salt are formed:

$$KOH + Al + H_2O = KAlO_2 + 3H$$

9. By the action of alkali metals on water. When a piece of metallic Sodium or Potassium is placed in water, it frees Hydrogen and forms an alkali-hydroxide. which dissolves in the water, decreasing in size gradually. If Potassium is used, the Hydrogen is ignited by the heat evolved; but not so when Sodium and cold water are taken.

$$Na + H_2O = NaOH + H$$

The water acquires an alkaline reaction from the hydroxide of the metal formed. In order to prepare Hydrogen by this method, roll a piece of metallic Sodium in a strip of wire-gauze, put into a cylinder filled with water and invert this over another vessel containing water (fig. 29).

History:

Hydrogen was observed by Paracelsus in the sixteenth century but the true discoverer was Cavendish (1776). Lavoisier was the one to show that water is a compound of Oxygen and Hydrogen.

COMPOUNDS OF HYDROGEN AND OXYGEN.

There are two compounds of Hydrogen and Oxygen:

I. Mon-oxide of Hydrogen, H—O—H.

II. Di-oxide of Hydrogen, H—O—O—H.

WATER (*aqua*) H_2O.

This is mon-oxide of Hydrogen, a colorless liquid boiling at 100° C. and freezing at 0° C. Its specific gravity is 1 at 4° C. but less at any other temperature. Ice is about 9-10ths as heavy as water, and floats upon it. Natural water is not chemically pure, but always contains salts in solution. These are mostly sulphates, chlorides and carbonates of Sodium, Potas-

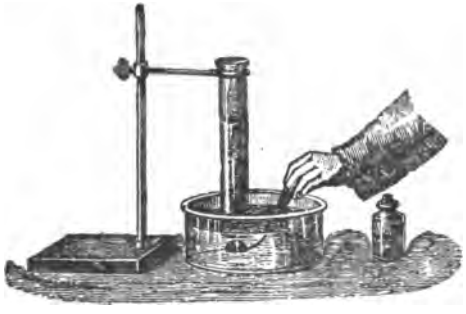


Fig. 29

sium, Calcium, Iron and Magnesium. Some of the carbonates (Calcium, Iron, Magnesium) are insoluble in water, but are retained in solution by the Carbon-dioxide, which is also present. Nitrates, nitrites, ammonia and organic substances may also be contained, but they render the water unfit for drinking purposes. if they exceed a certain limit. They indicate that the source of the water is polluted by decaying organic material. The presence of nitrites is not permitted in good water, and ammonia, nitrates and organic matter only in very small quantities. One liter of water should not leave more than half a gram of residue on evaporation.

On allowing a tumbler of water to stand, bubbles will be observed to form on the side of the glass; this is escaping Carbon-

dioxide being driven off by the water getting warm. When this disappears, the carbonates become insoluble and form a precipitate, coating the walls of the vessel.

If common water is used in boilers, incrustations are formed consisting of the precipitated impurities—Calcium, Magnesium and Iron salts, principally.

Hard water contains more of Lime and Magnesium salts than soft water, and is obtained from springs, wells, etc. It is the best kind for drinking, as the body needs some of the salts and the Carbon-dioxide renders it agreeable to the taste. It does not foam with soap, which is decomposed by the Lime and Magnesium salts.

Soft water is rain and river water. It is used for cleansing, and foams with soap.

If a water contains a large amount of certain inorganic salts, it is called a *mineral water*. Some of them have medicinal properties. They comprise *aperient waters,* as Hunyadi and Carlsbad waters; *alkaline waters,* like Vichy, Kissinger water; *chalybeate waters,* containing Iron; *lithium waters,* containing Lithium; and *sulphuretted waters.* Others, again, contain large quantities of Carbon-dioxide, as seltzer, apollinaris, etc,

Water is purified by distillation (*aqua destillata, U. S. P.*). One hundred volumes of water are subjected to distillation and the first ten volumes obtained are rejected, as they contain volatile impurities. The next eighty volumes are saved.

Water is one of the greatest chemical agents(the majority of chemical actions take place only in its presence). It unites with many other substances, and forms *hydroxides* of them.

Hydration is the process of uniting a body with water.

Dehydration is the process of removing water from a substance. *Dehydrating agents* take up water from other bodies, Sulphuric acid and Calcium-chloride are dehydrating agents.

DIOXIDE OF HYDROGEN, H_2O_2.

Hydrogenii dioxidum, U. S. P. *Peroxide of Hydrogen.*

This is a thick, syrupy liquid in the pure state, colorless and odorless but of a peculiarly bitter taste. It is easily soluble in

Agonia A 3

water. On standing, it soon splits into water and free Oxygen.

$$H_2O_2 = H_2O + O$$

This decomposition is caused by heat and may be accompanied by an explosion. A 3 percent solution is official as *aqua Hydrogenii dioxidi.* This is a colorless, odorless liquid of slight taste. It can be heated without decomposition only in a polished dish, and may then be distilled. It should be kept in loosely-stoppered bottles so that the liberated Oxygen can escape and explosions may be avoided.

It is a strong oxidising agent and an excellent bleacher, and is much used in industry. It is also a good antiseptic and disinfectant, giving up its Oxygen to the bacteria and killing them by excessive oxidation. With pus and blood it foams, caused by the escaping Oxygen.

Old oil paintings which have become dark by the conversion of white Lead into Lead-sulphide, can be restored to their original brilliancy by it, as the black Lead-sulphide is oxidised to white Lead-sulphate.

Peroxide of Hydrogen decolorises Potassium-permanganate, the Oxygen of both being freed. This is therefore one of the methods for the preparation of gaseous Oxygen. It appears in this reaction as a reducing agent, because it causes the Potassium-permanganate to give up its Oxygen. It also reduces the oxides of some metals, as Silver-oxide, Lead-dioxide, etc. For an explanation of the theory of this decomposition, see katalysers.

Preparation:

By treating Barium-dioxide with an acid, when Hydrogen-dioxide and a Barium salt of the acid are formed:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

Test for Hydrogen-dioxide:

Take some of the liquid to be tested in a test tube; add a drop of sulphuric acid and some ether, which forms a colorless layer on top. Then add a drop of a solution of Potassium-dichromate and shake; if peroxide of Hydrogen is present, the liquid will become dark blue.

SULPHUR.

SYMBOL, S; AT. MASS, 32; VALENCE, II: *with* O *also* IV, VI.

Source:

Sulphur is found in a free state in the neighborhood of volcanoes, mixed with sand , gravel, etc. It is then called *crude Sulphur*. The isle of Sicily is one of the principal sources.

It is found in a compound state in many minerals. A number of ores are compounds of Sulphur and metals. They are

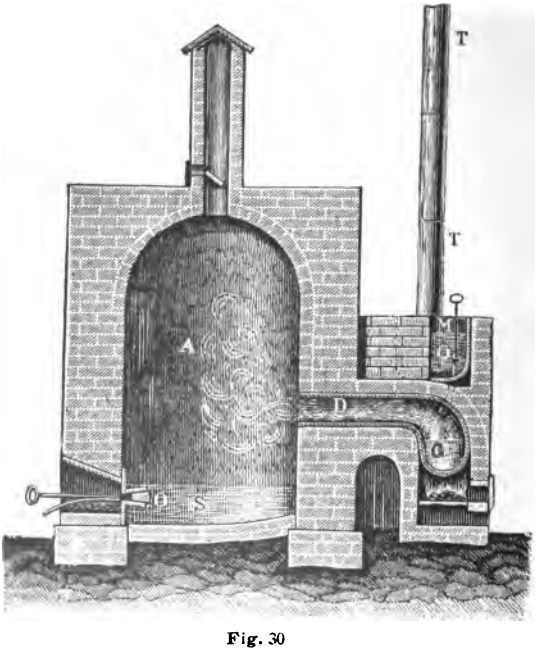


Fig. 30

called glances, blendes, kieses, etc., as Zinc-blende, a compound of Sulphur and Zinc. Some are called pyrites. Sulphur is also found in the mineral kingdom as sulphates, like gypsum (Calcium-sulphate). Sulphates are present in drinking water. It is further found in the animal and vegetable kingdom, espec-

ially in albuminous matter. When eggs are eaten with a silver spoon, it turns black on account of the action of the Sulphur which they contain.

Preparation:

Crude Sulphur is placed in kilns on top of the fuel, which when ignited, melts the Sulphur. This is then allowed to pass into cylindrical sand-tubes, where it solidifies and forms rolls, called *brimstone* or *rolls of Sulphur*. This brimstone is far from being pure, as it takes down some of the ashes and impurities with it. To rid it of these it is subjected to sublimation (fig. 30). The Sulphur is put into a large retort connected with a cool room, and the retort is heated. The Sulphur melts, then boils and the vapors pass into the cool room, where they are quickly solidified and fall down as a very fine powder, the *flowers of Sulphur* (*Sulphur sublimatum*). This has usually an acid reaction, as it contains some sulphuric acid. It also contains Arsenic-sulphide, which is always present in crude Sulphur (the Arsenic-sulphide is volatile and therefore sublimes with the Sulphur). In order to free the flowers of Sulphur of sulphuric acid and Arsenic-sulphide, it is washed with water containing ammonia—this dissolves the Arsenic-sulphide and neutralises the acid. Then it is washed with pure water and dried and is now known as *washed Sulphur* (*Sulphur lotum*).

A fourth kind used in Pharmacy is *lac Sulphur* (*Sulphur precipitatum*). It looks whiter than the other preparations, and is not as heavy. It is prepared by boiling flowers of Sulphur, water and slaked lime together for about two hours, forming a brown-colored solution. This is filtered and hydrochloric acid gradually added to the filtrate until the alkaline reaction has almost, but not entirely, disappeared; the Sulphur then precipitates. A smell of sulphide of Hydrogen is often observed, but this should not be the case if properly prepared.

Physical properties:

Sulphur is a yellow solid or powder, without odor or taste. It is insoluble in water, and only slightly soluble in alcohol or ether. It dissolves easily in Carbon-disulphide, and in Sulphur-chloride. It also dissolves, but with chemical change, when boiled with alkali-hydroxides or with oil. It melts at 115° C.

and forms a light yellow liquid; but when further heated, the color becomes darker and the consistency changes to that of a jelly. If heated still more, it becomes thinner again, but dark brown in color. It boils at 448° C., forming a yellow vapor.

If boiling Sulphur is suddenly chilled, as by pouring it quickly into cold water, it forms a rubber-like mass—this is *amorphous* or *plastic Sulphur*. This form gradually changes back to common Sulphur and gets hard again.
Plastic Sulphur is not soluble in Carbon-disulphide.

Sulphur can be obtained in two different crystalline shapes: *Octahedron* or *rhombic*, and *Prismatic*.

The rhombic form is the stable one—common Sulphur is the rhombic modification.

The prismatic form can be obtained by fusing, cooling until a crust is formed, breaking a hole through this and pouring, as explained under crystallisation.

Besides the above mentioned modifications of Sulphur, a fourth is known. This is the *white amorphous Sulphur*—a white powder, insoluble in Carbon-disulphide. It is present in flowers of Sulphur to the extent of about 5 percent. It may be obtained from this by dissolving out the flowers of Sulphur with Carbon-disulphide.

Chemical properties:

Sulphur burns with a blue flame, forming Sulphur-dioxide (SO_2). This gives a strong, pungent odor. Sulphur has many points in common with Oxygen. A number of metals burn in Sulphur vapors just as energetically as in Oxygen. The compounds thus formed are *sulphides*. In them Sulphur has a valence of 2.

There are acid sulphides and basic sulphides.

AN ACID SULPHIDE is one which theoretically unites with Hydrogen-sulphide and forms a sulpho-acid. To this class belong the sulphides of Arsenic, Antimony and Tin.

$$Sb_2S_5 + 3H_2S = \underset{\text{ortho-sulph-antimonic acid.}}{2H_3SbS_4}$$

A BASIC SULPHIDE is one which theoretically unites with Hydrogen-sulphide to form the real sulpho-base

$$K_2S + H_2S = \underset{\text{Potassium-sulph-hydrate}}{2KSH}$$

These compounds contain the univalent radicle (SH), which is called the SULPH-HYDRATE radicle, and compounds of it are SULPH-HYDRATES or HYDRO-SULPHIDES, just as the compounds of (OH) are called hydroxides or hydrates.

Sulpho-acids unite with sulpho-bases and form SULPHO-SALTS. with the separation of Hydrogen-sulphide.

$$H_3SbS_4 + 3NaSH = 3H_2S + Na_3SbS_4$$

Sodium-ortho-sulph-antimonate

OXIDES OF SULPHUR.

Sulphur forms several oxides, but there are two of primary importance:

SO_2—Sulphurous-oxide; and
SO_3—Sulphuric-oxide.

I. SULPHUROUS - OXIDE (*Sulphur-dioxide*) SO_2, is a colorless gas of pungent odor; it is very irritating to the eyes and also to the sense of smell. It dose not burn, and burning bodies introduced into it will not continue to burn. It is therefore used as a fire-extinguisher. It can easily be liquified by cold. It may be prepared by burning Sulphur, by roasting Sulphur-ores, or by boiling sulphuric acid with charcoal or Copper (see sulphurous acid). Sulphur-dioxide is soluble in water, and the solution is called sulphurous acid:

$$SO_2 + H_2O = H_2SO_3$$

This gas will blacken a strip of paper which has been dipped in a solution of Mercurous-nitrate.

There are two different classes of salts derived from sulphurous acid, in which the acid is:

1. The symmetrical sulphurous acid, HO—SO—OH.
2. The asymmetrical sulphurous acid, HO—SO_2—H.

These acids are isomers. In the former, Sulphur is 4-valent; in the latter Sulphur is 6-valent, and one OH in the formula of sulphuric acid is replaced by H.

Sulphurous Acid.

SULPHUROUS ACID (*Acidum sulphurosum*), H_2SO_3. This is a colorless liquid, having a strong smell on account of the Sulphur-dioxide present. It has a sour taste and acid reaction. The official form contains 6 percent of Sulphur-dioxide dissolved in water. If this acid is heated, it splits up into water and Sulphur-dioxide, which latter gas escapes:

$$H_2SO_3 = H_2O + SO_2$$

Sulphurous acid is a strong reducing agent; even in an open bottle it will take Oxygen from the air and change into sulphuric acid:

$$H_2SO_3 + O = H_2SO_4$$

Sulphurous acid is a strong decolorising and bleaching agent on account of this property to take up Oxygen. A red rose will be bleached to white if dipped in this acid. Paper and straw goods may be bleached with it, but will become yellow after a time. It decolorises a Potassium-permanganate and Iodine solution, and this fact may be used for its detection.

Sulphurous acid is a good antiseptic and disinfectant, killing the germs by robbing them of their Oxygen. It is used in many industries, and also in medicine.

If cooled to 0°C., it forms a kryo-hydrate.

Preparation. By boiling Carbon and sulphuric acid in the generating flask (fig. 9). The coal takes up the Oxygen from the sulphuric acid:

$$C + 2H_2SO_4 = CO_2 + 2H_2SO_3$$

The sulphurous acid formed splits on being heated into water and Sulphur-dioxide. The escaping gases—Carbon-dioxide and Sulphur-dioxide—are led to the wash-bottle and freed from impurities. From here they are conducted through bent glass tubes into the cold water of the receiving-bottle. Sulphur-dioxide, being soluble in water, forms sulphurous acid; while the insoluble Carbon-dioxide passes through the water and escapes.

Salts of sulphurous acid. These are called *sulphites.* They are white or colorless unless the metal colors them. The SO_3 ion is, then, colorless. The sulphites, with the exception of those of the alkalies, are insoluble or only soluble with difficulty. in water.

Tests for sulphurous acid and sulphites. 1. They decolorise Potassium-permanganate and Iodine solutions. 2 When a sulphite is treated with a stronger acid, it evolves a smell of burnt Sulphur, but the liquid remains clear.

The divalent radicle obtained by removing the hydroxyl groups from sulphurous acid is sometimes called THIONYL.

$S\ O_3$

II. Sulphuric Oxide.

II. SULPHURIC - OXIDE (*Sulphur-trioxide*), SO_3, is sometimes a colorless liquid, sometimes silk-like crystals, having a melting point which is about the ordinary temperature (this is why its state varies between liquid and solid). It is very volatile and fumes in air. When it is put in water, a hissing sound is noticed, and heat is produced. It forms sulphuric acid:

$$H_2\ O + SO_3 = H_2SO_4$$

Preparation. 1, By distilling di-sulphuric acid. 2, By passing a mixture of Sulphur-dioxide and Oxygen over heated platinised asbestos, which acts as a katalyser:

$$SO_2 + O = SO_3$$

Sulphuric Acid.

SULPHURIC ACID (*acidum sulphuricum*) H_2SO_4, is a thick, oily liquid. It is sometimes called *oil of vitrol.* It is heavier than water, its specific gravity being 1.826 (at 25° C.). Its boiling point is 338° C. On cooling, it forms colorless crystals. The official acid is 92.5 percent, the rest being water.

Sulphuric acid has a strong affinity for water, and when diluted with this solvent the solution gets very hot. If water is carelessly poured into sulphuric acid, it may cause an explosion. Therefore, to dilute, always pour the acid into cold water.

It is official in three forms:

1. The strong sulphuric acid (*acidum sulphuricum*) just described.
2. The diluted acid (*acidum sulphuricum dilutum*), which has a strength of 10 percent.
3. The aromatic sulphuric acid (*acidum sulphuricum aromaticum*), which contains about 20 percent by weight of sulphuric acid. It is prepared by diluting the acid with alcohol and flavoring with tincture of ginger and oil of cinnamon.

Chemical properties. It has two pre-eminent properties,

1. *Its great affinity for water.* It must be kept in tight containers, or it will absorb water from the air and become weaker. It is much used in desiccators for drying, the substance to be

dried being placed under a glass bell along with a dish of sulphuric acid.

When sulphuric acid is placed on wood (which is a carbohydrate—a compound of Carbon and water, $C + H_2O$) it darkens the wood, taking up the water and leaving the black Carbon. This fact may be applied to the detection of free sulphuric acid in commercial products. If vinegar containing free sulphuric acid be evaporated on a waterbath with some sugar (which is a carbo-hydrate), the residue is black. Sulphuric acid dehydrates many organic compounds.

2. *Its great affinity for metals.* It is one of the most powerful of all acids in this respect. When it comes in contact with a salt, it takes up the metal and frees the other acid. It is therefore used for the manufacture of acids from their salts. Nitric acid may be made by treating a nitrate with sulphuric acid; acetic acid by treating an acetate with sulphuric acid, and so on. If the acid to be prepared is volatile, the mixture of sulphuric acid and the salt is subjected to distillation, and the volatile acid is thus separated from the fixed sulphate formed. If the acid to be prepared is solid and not easily soluble in water, the mixture of sulphuric acid and the salt is cooled; the acid desired crystallises out and the sulphate formed remains in solution.

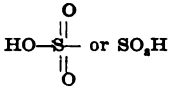
Preparation. Sulphuric acid is manufactured in large factories, where Sulphur is burned in furnaces to form SO_2 gas. This is passed into a room the walls of which are covered by plates of Lead. Jets of steam are discharged into this room continuously; this, with the Sulphur-dioxide, forms sulphurous acid (H_2SO_3). Nitric acid is led into the room through a glass tube, and flows onto a terrace made of earthenware. The nitric acid, running down from one step to another, exposes much surface and gives up Oxygen to the sulphurous acid, changing it into sulphuric. The nitric acid is reduced to nitrous acid (HNO_2), but this takes up O from the current of air which the draught of the furnace maintains, and forms nitric acid again. This in turn oxidises a fresh portion of sulphurous acid, and so the process keeps on. Thus small quantities of

nitric acid are all that are needed to oxidise large amounts of sulphurous acid.

The theory of the formation of sulphuric acid given here is not quite correct, but the correct theory requires a greater knowledge of chemistry than the student has gained as yet.

The sulphuric acid collected on the bottom of the Lead-walled chamber is called *chamber sulphuric acid.* It has a strength of from 60 to 68 percent. In order to make it stronger, it is evaporated in Lead pans until it has a percentage of about 75. This is known as *pan sulphuric acid.* Finally, it is evaporated in Platinum or glass vessels until its strength is 92.5 percent.

The group or radicle which remains when one OH group is removed from sulphuric acid is called the SULPHONIC ACID RADICLE. It is univalent, and has the formula



The divalent radicle (SO_2) obtained by removing both OH groups is called SULPHURYL.

The salts of sulphuric acid are *sulphates.* These are colorless, unless the metal colors them (the SO_4 ion is colorless). They are all soluble in water except those of Barium, Strontium, Calcium and Lead.

Tests for sulphuric acid and sulphates. Add to the solution to be tested some Barium-chloride, and get a white precipitate which is insoluble in any acid if sulphates or sulphuric acid are present.

Di-sulphuric Acid, $H_2S_2O_7$.

DI-SULPHURIC ACID, $H_2S_2O_7$. This is also called *fuming, Nordhausen, or pyro-sulphuric acid.* It is a thick, heavy liquid, fuming in air. When cooled it solidifies. It may be considered as a compound of sulphuric acid and Sulphur-trioxide:

$$H_2SO_4 + SO_3 = H_2S_2O_7$$

It may be considered as consisting of two sulphonic acid groups, linked together by an Oxygen atom:

$$HSO_3—O—SO_3H, \text{ or } H_2S_2O_7$$

If it is distilled, the Sulphur-trioxide, having a lower boiling point, goes over first—leaving the sulphuric acid. When mixed

with water it hisses, generates great heat, and forms sulphuric acid by the union of the Sulphur-trioxide with water:

$$H_2S_2O_7 + H_2O = 2H_2SO_4$$

Preparation. 1, By heating Ferrous-sulphate to red heat, when di-sulphuric acid distils over and Ferric-oxide, a reddish-brown mass, remains in the retort.

2, By passing SO_3 vapors into concentrated sulphuric acid

$$H_2SO_4 + SO_3 = H_2S_2O_7$$

The modus operandi is as follows: Strong sulphuric acid is led into retorts heated to redness. The sulphuric acid splits

$$H_2SO_4 = H_2O + SO_2 + O.$$

These gases are deprived of water by passing them through a coke tower, through which strong sulphuric acid flows and absorbs moisture. On leaving the coke tower, the mixture consists of SO_2 and O only. These are passed over hot porous Platinum, which, by its katalytic action, causes them to unite and form SO_3. This is passed into concentrated sulphuric acid, and di-sulphuric acid results.

The salts of di-sulphuric acid are called *di-sulphates* or *pyro-sulphates.* Sodium-pyrosulphate may be obtained by heating Sodium-bisulphate:

$$2NaHSO_4 = Na_2S_2O_7 + H_2O$$

Thiosulphuric Acid.

THIOSULPHURIC ACID (*hyposulphurous acid*), $H_2S_2O_3$, may be considered as sulphurous acid with an additional atom of Sulphur:

$$H_2SO_3 + S = H_2S_2O_3$$

Or, more desireably, as sulphuric acid in which one Oxygen atom is replaced by a Sulphur atom; or as sulphuric acid in which one OH group is replaced by an SH group:

$HO—SO_2—OH$, sulphuric acid.

$HO—SO_2—SH$, thiosulphuric acid.

It does not exist in the free state, splitting, as soon as formed, into sulphurous acid and Sulphur; salts of the acid are known, however, and are called *thiosulphates* or *hyposulphites*. The most important of these is the Sodium-thiosulphate (Sodium-hyposulphite—the hypo of photography), $Na_2S_2O_3$. It appears in the form of colorless crystals, soluble in water. It is prepared by boiling Sodium-sulphite together with water and Sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3$$

Tests for thiosulphuric acid and thiosulphates. 1, Potassium-permanganate or Iodine solutions are decolorised by them. 2, If a thiosulphate is treated with a stronger acid, it evolves an odor of Sulphur-dioxide and gives a precipitate of Sulphur. Thiosulphuric acid is set free, and splits into Sulphur and sulphurous acid:

$$H_2S_2O_3 = H_2SO_3 + S$$

There are several other acids of Sulphur of lesser importance. The known acids of Sulphur are as follows:

1. HYPOSULPHUROUS ACID (true): derived from a hypothetical oxide of Sulphur in which Sulphur is bi-valent.

$$SO + H_2O = H_2SO_2$$

2. SULPHUROUS ACID: the symmetrical and the asymmetrical, as explained.

3. SULPHURIC ACID: which we have discussed.

4. THIOSULPHURIC ACID (wrongly named hyposulphurous acid): $H_2S_2O_3$. It may be considered as sulphuric acid in which one OH is replaced by SH.

The other acids of Sulphur may be considered as formed by two sulphonic acid groups,—SO_3H, linked together directly or indirectly by atoms of Sulphur or atoms of Oxygen.

ACIDS FORMED BY DIRECT LINKING.

5. DITHIONIC ACID:

$$HSO_3—SO_3H \text{ or } H_2S_2O_6$$

ACIDS FORMED BY INDIRECT LINKING.

(a). By Sulphur atoms.

6. TRI-THIONIC ACID:

$$HSO_3—S—SO_3H \text{ or } H_2S_3O_6$$

7. TETRA-THIONIC ACID:

$$HSO_3—S—S—SO_3H \text{ or } H_2S_4O_6$$

This is of rather more importance, as its Sodium salt is formed when Sodium-thiosulphate is treated with Iodine—the Iodine being decolorised. This reaction is important in volumetric analysis.

8. PENTA-THIONIC ACID:

$$HSO_3—S—S—S—SO_3H \text{ or } H_2S_5O_6$$

(b). By Oxygen atoms.

9. DI-SULPHURIC ACID (pyro-sulphuric acid):

$$HSO_3—O—SO_3H \text{ or } H_2S_2O_7$$

10. PER-SULPHURIC ACID:

$$HSO_3—O—O—SO_3H \text{ or } H_2S_2O_8$$

This acid is formed at the positive pole when an electric current is passed through cooled 40 percent sulphuric acid. It is a very strong oxidising, bleaching and disinfecting agent, like Hydrogen-peroxide. Its salts are used for the same purpose.

Hydrogen Sulphide.

HYDROGEN SULPHIDE (*Hydrogenii Sulphidum*), H—S—H, also known as *sulphuretted Hydrogen,* is a colorless gas of a very disagreeable odor, and is very poisonous. It is soluble in water, to which it imparts its characteristic odor. It is weakly acid in reaction and properties. Its solution is called sulphydric acid. It should be kept in completely filled, tightly closed bottles, as it readily oxidises and forms water and a precipitate of Sulphur:

$$H_2S + O = H_2O + S$$

It is a strong reducing agent. Chromic acid and permanganic acid are reduced by it, the Hydrogen-sulphide taking up a part of their Oxygen, and forming water and Sulphur as above. Ferric salts are reduced to Ferrous salts by its action on them. If it is brought together with Sulphur-dioxide, the latter is reduced and Sulphur precipitates out:

$$SO_2 + 2H_2S = 2H_2O + 3S$$

H_2S is combustible, burning with a blue flame and forming water and Sulphur-dioxide. If there is an insufficient amount of Oxygen for complete combustion, the Hydrogen burns and forms water, while the Sulphur separates out.

Occurrence. It is found in nature in volcanoes; it is also found in sewer gas, the gases of the intestines, and where organic matter decays.

Preparation: It is prepared by treating Iron-sulphide (FeS) with dilute sulphuric acid, forming Ferrous-sulphate and Hydrogen-sulphide:

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

Uses. Hydrogen-sulphide is one of the most important

chemical reagents—it is the principal test for metals. When bright metals come in contact with the gas they are blackened. This is the chief factor in the tarnishing of jewelry.

If H_2S is passed through a solution of a metal, the metal is precipitated as a sulphide:

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

According to their conduct when treated with Hydrogen-sulphide, the metals may be divided into four classes:

1. Those metals which are precipitated by H_2S, regardless of whether the solution has an acid or an alkaline reaction (Mercury, Lead, Silver, Cadmium, Bismuth, Copper).

2. Metals which H_2S precipitates only in acid solution (Arsenic, Antimony, Tin, Gold, Platinum).

3. Metals which H_2S precipitates only in alkaline solution (Iron, Zinc, Manganese, Cobalt, Nickel).

4. Metals which H_2S does not precipitate (Sodium, Potassium, Ammonium, Lithium, Barium, Strontium, Calcium, Magnesium).

This action of Hydrogen-sulphide on metals permits not only the detection of their presence, but also offers a means of separating them. Suppose, for instance, it is desired to separate Zinc and Magnesium from a solution containing a mixture of their sulphates. Ammonium-chloride and ammonia water are added to render them alkaline, and then Hydrogen-sulphide is passed through the solution; the Zinc forms a white precipitate, while the Magnesium salt remains in solution.

Sulphur and Hydrogen form another compound, called Hydrogen-persulphide. The formula is not definitely determined as yet, but it is one of the following:

H—S—S—H
H—S—S—S—H
H—S—S—S—S—H
H—S—S—S—S—S—H

Very probably the last formula is the correct one. It is a heavy oily liquid of peculiar odor, easily decomposed into Sulphur and Hydrogen-sulphide.

SELENIUM (Se) and TELLURIUM (Te).

These two elements are similar in their chemical properties to Sulphur—Tellurium being rather more metal-like. Their valence is the same as that of Sulphur, the formulae of their compounds are analagous to those of the Sulphur compounds; the properties of these compounds also bear a close relationship.

The four elements, Oxygen, Sulphur, Selenium and Tellurium are related to each other and form a natural group.

THE HALOGEN GROUP.

FLUORINE, AT. MASS 18.9—a *pale green gas.*

CHLORINE, AT. MASS 35.18—*a yellowish-green gas.*

BROMINE, AT. MASS 79.36—*a brown, heavy liquid.*

IODINE, AT. MASS 125.9—*a shiny black solid.*

The valence of all four is generally 1, and with Oxygen 1, 3, 5 and 7; but as Fluorine does not unite with Oxygen, it has a valence of 1 only.

The name 'halogen' means salt-builder. These elements unite directly with the metals and form salts, without the intervention of Oxygen. They also form acids without the aid of Oxygen, and these are called the *hydro-acids* (HFl, HCl, HBr and HI). These acids, in anhydrous condition, are colorless gases, with the exception of Hydrofluoric acid, which is a liquid of low boiling point (19° C.). They fume in air by reason of the moisture they absorb, which condenses and forms a mist. They have an irritating smell and are freely soluble in water.

Halogen elements have great affinity for Hydrogen and metals. This property is most marked in Fluorine, next Chlorine, then Bromine and Iodine has the least affinity. If an iodide is treated with one of the other halogen elements, the Iodine is displaced and the compound of the other halogen formed:

$$HI + Cl = HCl + I$$

In the presence of water, the halogens are strong oxidising

agents. They unite with the Hydrogen of the water, liberating the Oxygen:

$$2Cl + H_2O = 2HCl + O$$

They are for this reason good disinfectants and bleaching agents, because the Oxygen freed can oxidise germs and coloring matter.

Their affinity for Oxygen is small, and their Oxygen compounds are unstable and usually explosive. Fluorine has the least affinity for Oxygen—no compound of the two being known. Chlorine has a little more affinity for Oxygen, with which it unites in some instances. Bromine has more affinity for Oxygen than has Chlorine, and Iodine the most of the halogen elements. Even this is comparatively small.

CHLORINE.

SYMBOL, Cl; AT. MASS, 35.18; VALENCE I: *with* O *also* III, V VII.

Physical properties:

Chlorine is a yellowish green gas of disagreeable odor, very irritating to the eyes and nostrils. It is dangerous to inhale it. It can be liquified by cold and compression (see fig.11). It is somewhat soluble in water, the liquid obtained being called Chlorine water (*aqua Chlori*). This solution should be kept in dark bottles, as it is decomposed by light into hydrochloric acid and free Oxygen:

$$2Cl + H_2O = 2HCl + O$$

Chemical properties:

Chlorine does not burn, as its affinity for Oxygen is small; but it has a great affinity for metals and Hydrogen. Many metals ignite spontaneously when brought into Chlorine, and are converted into chlorides. The affinity between Hydrogen and Chlorine is increased by sunlight . A mixture of Hydrogen and Chlorine may be preserved for a considerable length of time if kept in a dark place; in sunlight it explodes. This mixture is called *Chlorine detonating gas.*

Chlorine is used very much for oxidation and for bleaching.

For this latter purpose it is especially used in the linen and cotton industry. Bleaching performed with Chlorine is more permanent than that brought about by the use of sulphurous acid.

Chlorine is also a good disinfectant and antiseptic, as it liberates Oxygen and thus kills the germs. Its affinity for Hydrogen is so great that it will take Hydrogen from its compounds. If Chlorine and Hydrogen-sulphide act on each other, hydrochloric acid and free Sulphur are formed:

$$H_2S + 2\ Cl = 2\ HCl + S$$

Oil of turpentine, a compound of Hydrogen and Carbon, is immediately carbonised by Chlorine.

When strong Chlorine-water is cooled below 0° C., yellow scale-like crystals are formed. These are a compound of Chlorine and water, called *Chlorine hydrate*:

$$Cl + 4H_2\ O$$

On being warmed, this splits into Chlorine gas and water.

Occurrence:

Chlorine is not found in the free state on account of its great affinity for Hydrogen and the metals, but in compounds, especially as Sodium-chloride (NaCl) or common salt, which is present in sea-water to the extent of 2.7 percent. It is also mined as rock-salt. The salt mines were seas in by-gone ages, and were later evaporated.

Preparation:

It may be obtained by treating hydrochloric acid with powerful oxidising agents:

$$2HCl + O = H_2O + 2Cl$$

Peroxide of Hydrogen, Manganese-dioxide, Lead-oxide, Barium-dioxide, nitric acid, Potassium-permanganate, chromic acid Potassium-dichromate or any other strong oxidising agent may be used. Below are a few methods of preparation.

1. Treat Manganese-dioxide with hydrochloric acid. Chlorine,

Manganous-chloride and water are formed:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl$$

2. Boil black oxide of Manganese with common salt and sulphuric acid. Sodium-sulphate, Manganous-sulphate, water and Chlorine are formed:

$$MnO_2 + 2NaCl + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + 2Cl$$

3. Heat Potassium-dichromate with hydrochloric acid. Potassium-chloride, Chromium-chloride , water and Chlorine result:

$$K_2Cr_2O_7 + 14\,HCl = 2KCl + 2CrCl_3 + 7H_2O + 6Cl$$

The following is the U. S. P. method for the extemporaneous preparation of Chlorine-water (*liquor Chlori compositus*):

Potassium-chlorate is introduced into a large bottle, hydrochloric acid diluted with about an equal volume of water added, and the flask gently warmed. If the flask becomes full of the green Chlorine gas, cold distilled water is added in two separate portions through a funnel plugged with wet cotton. After each addition the flask is closed and well shaken to ensure solution of the gas.

History:

Chlorine was discovered by Scheele in Sweden, 1774. It was first thought to be a compound, but Gay-Lussac and Thenard in France and Davy in England proved it to be an element.

Chloride of Hydrogen (HCl).

HYDROCHLORIC ACID, (*Acidum Hydrochloricum*), also called *muriatic acid* is a colorless gas of pungent odor. It is irritating to the bronchial tubes, nasal passages and eyes. In moist air it evolves white fumes. It is very soluble in water, one liter of which will dissolve more than five hundred liters of the gas at 0° C. The solution of the gas in water is colorless, has a sour taste and an acid reaction and is called *hydrochloric* or *muriatic acid.* It has tho same chemical properties as the gas.

Two solutions of HCl are official, a strong solution containing

31.9 percent, *acidum hydrochloricum*; and a weaker one, containing 10 percent of the hydrochloric acid gas in water, *acidum hydrochloricum dilutum.* Commercial or crude hydrochloric acid varies in strength from 18 to 25 percent. It contains impurities—Iron being almost always present, and lending the solution a yellow color.

When a solution of hydrochloric acid weaker than 20.24 percent is distilled, only watersteam passes off until the residue has a strength of 20.24 percent; then an acid of just that percentage distils. If an acid stronger than 20.24 percent is distilled, pure gas goes over till the temperature is 110° C. and the strength of the liquid is 20.24 percent; then a liquid distils of exactly this percentage.

Hydrochloric acid gas is not burnable. When the gas or solution is treated with a strong oxidising agent, it forms water and Chlorine:

$$2HCl + O = H_2O + 2Cl$$

Preparation. By treating common salt with sulphuric acid. Sodium-sulphate and hydrochloric acid are formed:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2\ HCl$$

The hydrochloric acid gas is then passed into water, where it dissolves. To obtain pure acid, glass vessels are used. In factories, the salt and sulphuric acid are brought together in heated Iron cylinders lined with Lead. The gas is further conducted into a tower filled with pieces of coke, over which a constant stream of water is maintained. The ascending gas and the descending water come in contact, and the gas is dissolved. The solution is led out from the bottom of the tower.

Salts of hydrochloric acid. These are called *chlorides* or *hydrochlorides.* The latter name is only used for the chlorides of the alkaloids. All chlorides are colorless unless the metal colors them. They are all soluble in water, with the exception of Silver-, Mercurous- and Lead-chlorides—the latter being somewhat soluble, especially in hot water.

A few rarer chlorides are insoluble in water, as Thallium-chloride.

Tests for chlorides and hydrochloric acid. Add to the solu-

tion to be tested a Silver-nitrate solution. In the presence of hydrochloric acid, a white precipitate which is soluble in ammonia and reprecipitated by nitric acid is obtained.

Oxygen compounds of Chlorine.

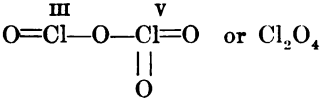
According to its valence with Oxygen, Chlorine should form four oxides:

Cl_2O—Monoxide of Chlorine, hypochlorous-oxide.
Cl_2O_3—Trioxide of Chlorine, chlorous-oxide.
Cl_2O_5—Pentoxide of Chlorine, chloric oxide.
Cl_2O_7—Heptoxide of Chlorine, perchloric-oxide.

Only the first of these theoretical oxides is known; but an additional one, which may be regarded as a compound of Chlorine-trioxide and Chlorine-pentoxide, exists:

$$Cl_2O_3 + Cl_2O_5 = Cl_4O_8$$

This is usually written Cl_2O_4, and called Chlorine-tetroxide or Chlorine-peroxide. The graphical formula of this compound contains one atom of trivalent and one atom of pentavalent Chlorine, linked by a bivalent Oxygen atom—the other valence being also saturated by Oxygen:



or Cl_2O_4

Chlorine-monoxide is a yellow gas which liquifies at 5° C. It is explosive and unstable.

Chlorine-tetroxide is a yellowish gas liquifying easily. It is also explosive and unstable.

Both have disagreeable odors and can be easily liquified by cooling in a freezing mixture of ice and salt. They then form reddish-brown liquids.

The first four of these theoretical oxides unite with water and form acids:

$$Cl_2O + H_2O = 2HClO, \text{ hypochlorous acid.}$$
$$Cl_2O_3 + H_2O = 2HClO_2, \text{ chlorous acid.}$$
$$Cl_2O_5 + H_2O = 2HClO_3, \text{ chloric acid.}$$
$$Cl_2O_7 + H_2O = 2HClO_4, \text{ perchloric acid.}$$

Three of these acids are known and can be prepared—the hypochlorous, chloric and perchloric acids; while the chlorous acid has not as yet been obtained. These acids are unstable, and readily break down into the oxide and water: the oxide at once split into Chlorine and Oxygen. They are therefore oxidising agents. Hypochlorous and chloric acids are the two of most importance.

Hypochlorous acid (*HClO*).

HYPOCHLOROUS ACID (*acidum hypochlorosum*), Cl—O—H, is only met with in solution in water. It is a colorless or pale yellow liquid, having the odor of Chlorine, which it readily frees. It is a good bleaching agent, yielding Oxygen and Chlorine, which both effect this purpose. In diluted state it can be distilled. Its salts, the *hypochlorites,* also have the odor of Chlorine because they are partially broken down by the carbonic acid of the air. Thus hypochlorous acid is even weaker than carbonic acid. Its most important salt is Calcium-hypochlorite, which is contained in the chlorinated lime (chloride of lime, *calx chlorata*). This is a mixture of Calcium-hypochlorite, Calcium-chloride and Calcium-hydroxide.

It is now thought that chloride of lime is a compound derived by substituting the two Hydrogen atoms contained in one molecule of each of HCl and HClO by a bivalent atom of Calcium.

Cl— —Ca— —ClO

It is prepared by passing Chlorine gas into rooms containing slaked lime, which absorbs the Chlorine. It is a white powder having a strong odor of Chlorine. It absorbs moisture when exposed to air, and should therefore be kept well closed. It is only partially soluble in water; the Calcium-hydroxide being the portion that is only slightly soluble. On boiling with water,

it is converted into Calcium-chlorate and Calcium-chloride, and thus rendered inactive.

All salts of hypochlorous acid are thus decomposed by boiling. Sodium-hypochlorite forms Sodium-chlorate and Sodium-chloride.

When treated with an acid, it evolves Chlorine; and, according to the requirements of the U. S. P., it should yield not less than 30 percent (by weight) of this gas. It is used in place of Chlorine for bleaching and disinfecting, being more convenient to handle. For this reason it is also called *bleaching lime* or *bleaching powder.*

Other hypochlorites may be prepared by passing Chlorine gas into cold solutions of the strong bases (as Potassium-hydroxide). The chloride of the metal is also formed:

$$2KOH + 2Cl = KCl + KClO + H_2O$$

Chloric acid ($HClO_3$)

CHLORIC ACID (*acidum chloricum*) is a colorless, oily liquid. As it splits easily into Chlorine, water and Oxygen, it is a strong oxidising and bleaching agent. It ignites Phosphorus, rubber, Sulphur, sugar and paper when brought in contact with them.

The salts of chloric acid, the *chlorates,* are colorless unless the metal colors them. All are soluble in water. Silver-nitrate does not give a precipitate with solutions of chlorates (differential test between chlorides and chlorates). On being heated, the chlorates free Oxygen and become chlorides:

$$KClO_3 = KCl + 3O$$

First they are converted by heat into a mixture of chloride and perchlorate, as they do not give up all Oxygen at once:

$$2KClO_3 = KClO_4 + KCl + 2O$$

When the heat is further increased, the perchlorate gives up its Oxygen and forms the chloride:

$$KClO_4 = KCl + 4O$$

If a chlorate is treated with hydrochloric acid, it forms a chloride, water and Chlorine; which latter, being a gas, escapes. If a chlorate is triturated with burnable substances like coal,

sugar, tannic acid, etc., it explodes with terriffic force. Care must therefore be exercised in mixing chlorates with burnable substances. This should never be done by triturating in the ordinary way, but by mixing between soft paper or with other soft instrument.

Preparation of chlorates. 1, By boiling hypochlorites, which split into chlorates and chlorides. 2, By passing Chlorine gas into a boiling solution of a strong base:

$$6KOH + 6Cl = KClO_3 + 5KCl + 3H_2O$$

PERCHLORIC ACID ($HClO_4$) is a colorless, fuming, heavy liquid. If poured into water, it produces a hissing sound. It is a strong oxidising agent, and may even explode when brought in contact with burnable substances. Its salts, the PERCHLORATES, are prepared by heating the chlorates.

COMPOUNDS OF CHLORINE AND SULPHUR.

Sulphur-dichloride (SCl_2)—in which Sulphur has a valence of 2.

Sulphur-tetrachloride (SCl_4)—in which Sulphur has a valence of 4.

Sulphur-monochloride (Cl—S—S—Cl): Two bivalent atoms of Sulphur link together with a single bond, and the remaining valences are filled with Chlorine.

It is a reddish-brown liquid, of sharp odor. It can be distilled. It is heavier than water, which it decomposes. It fumes in air and dissolves Sulphur. It may be prepared by passing Chlorine gas over molten Sulphur.

Chlorine also unites with the Thionyl, Sulphuryl, and Sulphonic acid radicles, forming the following compounds:

Thionyl-chloride, $(SO)Cl_2$
Sulphuryl-chloride $(SO_2)Cl_2$
Chloro-sulphonic acid, $Cl—SO_3H$

BROMINE (Bromum).

SYMBOL, Br; AT. MASS, 79.36; VALENCE, I, *with* O *also* III, V, VII.

Bromine is a brown liquid—the only liquid element beside Mercury. It has a very disagreeable odor, as its name, derived from the greek word meaning stench, implies. It is irritating to the eyes, nose and respiratory passages, and care should be taken to avoid inhaling any of its fumes. It is often kept in bottles jacketed by a tin can containing Fuller's earth, silicious earth, or the like. On being cooled, it solidifies and crystallises. At ordinary temperatures it gives up brown vapors, and boils at 63°

C. It is somewhat soluble in water, the solution thus obtained being called *Bromine-water*. It is soluble in ether, Carbon-disulphide and chloroform, forming brown solutions. It imparts an orange coloration to starch paste.

Chemical properties:

Bromine does not burn, on account of its slight affinity for Oxygen. It unites energetically with Hydrogen and the metals, although not with the strength of Chlorine. If Chlorine is passed through a solution of a bromide, the Chlorine takes up the metal and liberates the Bromine:

$$KBr + Cl = KCl + Br$$

Bromine is a strong oxidising, bleaching and disinfecting agent, taking up the Hydrogen from water and liberating the Oxygen.

Occurrence:

Bromine is found to a small extent in combination with Sodium and other metals, in sea-water and also in certain springs. It is also contained as an impurity in rock salt from certain salt deposits, especially as Sodium-bromide and Magnesium-bromide from mines in the United States and at Strassfurth, Germany. When the solution of such salts is partially evaporated, the common salt separates but the bromides of Sodium and Magnesium remain in the mother liquor.

Preparation:

1. By passing Chlorine gas through a solution of a bromide.

$$KBr + Cl = KCl + Br$$

2. By distilling Sodium-bromide with black oxide of Manganese and sulphuric acid. Sodium-sulphate, Manganese-sulphate, water and Bromine are formed:

$$2NaBr + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2Br$$

History:

Bromine was discovered by Ballard in France, 1826, in sea-water.

Bromide of Hydrogen (HBr).

HYDROBROMIC ACID (*acidum hydrobromicum*), is a colorless, gas of pungent odor, very soluble in water. A 10 percent solution is official under the name *acidum hydrobromicum dilutum.* Hydrobromic acid closely resembles hydrochloric acid. When heated with strong oxidising agents, it splits into water and free Bromine:

$$2HBr + O = H_2O + 2Br$$

Preparation. Bromide of Potassium is distilled with sulphuric acid, and Potassium-sulphate and hydrobromic acid gas result. The gas is passed into water, where it dissolves. Phosphoric acid may be substituted for sulphuric acid, which decomposes the hydrobromic acid to a certain degree and colors it brown or yellow:

$$2KBr + H_2SO_4 = K_2SO_4 + 2HBr$$

The most convenient method of preparing hydrobromic acid is as follows: pour some water in a flask, and place a piece of Phosphorus in it; add Bromine as the mixture cools; then finally distil. The Phosphorus unites with the Bromine, forming Phosphorus-bromide (PBr_3 or PBr_5, according to the relative amounts of Bromine and Phosphorus present):

$$P + 5Br = PBr_5$$

The water decomposes the Phosphorus-bromide forming hydrobromic acid and an acid of Phosphorus (phosphorous or phosphoric according to the bromide present):

$$PBr_5 + 4H_2O = H_3PO_4 + 5HBr$$

The salts of hydrobromic acid are called *bromides,* and those of the alkaloids *hydrobromides.* They are colorless unless colored by the metal; Silver-bromide has a slight yellow tinge. All are soluble in water, with the exception of Silver-, Lead- and Mercurous-bromide.

Tests for hydrobromic acid and bromides. 1, To the solution to be tested, add some chloroform and Chlorine-water; if hydrobromic acid or a bromide is present, the chloroform is colored brown or orange (free Bromine). 2, Add a solution of Silver-nitrate to the solution to be tested; in the presence of a bromide

this yields a precipitate insoluble in dilute nitric acid but soluble with some difficulty in ammonia water.

COMPOUNDS OF BROMINE AND OXYGEN.

These are very similar to the corresponding ones of Chlorine. The known oxy-acids are:

$HBrO$, hypobromous acid
$HBrO_3$, bromic acid
$HBrO_4$, perbromic acid, is also said to have been prepared.

IODINE(Iodum).

SYMBOL, I; AT. MASS, 125.9; VALENCE, I, *with O also* III, V, VII.

Physical properties:

Iodine is a solid, consisting of dark-colored scales of metallic lustre; it is, however, one of the most characteristic non-metallic elements. Its odor slightly resembles that of Chlorine. On being heated, it melts, and if sufficient heat is applied it sublimes forming violet vapors. The name of the element is derived from the greek word for violet.

Iodine is only slightly soluble in pure water, but much more so if the water contains Potassium-iodide. Such a solution is official as *liquor iodi compositus* or *Lugol's solution;* it contains 5 percent of Iodine, 10 percent of Potassium-iodide, and water. Iodine is soluble in alcohol up to 7 percent, and an alcoholic solution is official as *tinctura Iodi.* Iodine is also soluble in ether.

The above solutions are of a brown color. Those in chloroform and di-sulphide of Carbon are violet.

Chemical properties:

Iodine does not burn, on account of its slight affinity for Oxygen. Its affinity for Hydrogen and the metals is strong, though not so marked as that of Bromine and Chlorine. If an iodide is treated with either Bromine or Chlorine, it is split up:

$$KI + Br = KBr + I$$

Iodine can be decolorised by any reducing agent in the presence of water; the reducing agent takes up the Oxygen of the water, while the Hydrogen combines with the Iodine to form colorless hydroiodic acid:

$$2I + H_2O + H_2SO_3 = 2HI + H_2SO_4$$

The hydroiodic acid and the sulphuric acid formed in this instance are both colorless, and so is their mixture. Ammonia also decolorises Iodine solutions, and is used to remove Iodine-stains. Sodium-hyposulphite will also do this.

Sodium-iodide and Sodium-tetra-thionate are produced by the reaction

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$$

The decolorised tincture of Iodine is made by adding ammonia water or Sodium-hyposulphite to the common tincture of Iodine. It is much used in medicine, as the other forms brown stains. As the free Iodine is changed to hydroiodic acid or iodides, it is probable that it does not have the medicinal effect sought after.

When Hydrogen-sulphide gas is passed through water in which finely-powdered Iodine is suspended, it is decomposed and forms Hydrogen-iodide and a precipitate of Sulphur:

$$H_2S + 2I = 2HI + S$$

The solution is thus decolorised.

Iodine colors starch blue. When the blue mass is boiled with water, the color disappears; but on cooling it is again seen.

Source:

Iodine is found in sea-water as Sodium-iodide, Magnesium-iodide, etc.; it is taken up from the water and stored by many sea-plants. On the coasts of Scotland and of France, gathering certain seaweed rich in Iodine is a recognised industry. The ashes of this crude material for the preparation of Iodine is called *kelp* in Scotland and *varec* in France.

Iodine is also found as an impurity in Chili saltpeter (Sodium-nitrate) in the form of Sodium-iodate. In the human body Iodine is present in the thyroid gland.

Preparation:

1. By passing Chlorine gas through a solution of the ashes of seaweeds, forming Sodium-chloride and free Iodine:

$$NaI + Cl = NaCl + I$$

2. By heating the ashes of the sea-plants with black oxide of Manganese and sulphuric acid. Sodium-sulphate, Maganese-sulphate, water and free Iodine are formed:

$$2NaI + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + 2I$$

3. By passing sulphurous acid through a solution of Chili saltpeter.

The Iodine contained in Chili saltpeter is present in the form of Sodium-iodate, $NaIO_3$, which is reduced by the sulphurous acid and free Iodine and sulphuric acid are formed. The sulphuric acid unites with the Sodium, forming sulphate or bi-sulphate of Sodium:

$$2NaIO_3 + 5H_2SO_3 = 2I + 2NaHSO_4 + 3H_2SO_4 + H_2O$$

A fourth method of preparing free Iodine from kelp or from iodides is based on the fact that Iodine is liberated when an iodide is heated with a Ferric salt, which is itself reduced to the Ferrous condition:

$$FeCl_3 + KI = FeCl_2 + KCl + I$$

The Iodine thus obtained is purified by repeated sublimation.

History:

Iodine was discovered by Courtois in France, 1811.

Test for free Iodine: It colors starch blue.

Hydrogen-iodide (HI).

HYDRIODIC ACID (*acidum hydriodicum*) is a colorless gas of sharp odor, freely soluble in water. The solution is called *hydriodic acid;* it has a strong, sour taste and an acid reaction. It is not very stable, as it is an endothermic compound and readily splits into Hydrogen and Iodine. It is therefore used as reducing agent, because its Hydrogen combines with the Oxygen of other bodies when liberated. When treated with an oxidising agent, hydriodic acid forms water and free Iodine:

$$2HI + O = H_2O + I$$

and becomes brown in color. In prescriptions, it should never be

mixed with oxidising agents like nitric acid, Hydrogen-peroxide, etc.

It is officinal as *acidum hydriodicum dilutum* (10 percent), and *syrupus acidi hydriodici* (1 percent). The latter is a mixture of the acid with simple syrup.

Preparation. 1, By treating a solution of Potassium-iodide with tartaric acid. Potassium-bitartrate precipitates, while hydriodic acid goes into solution. The U. S. P. uses the following modification: Potassium-iodide and Potassium-hypophosphite are dissolved in water. Tartaric acid is dissolved in diluted alcohol. The two solutions are mixed and placed on ice for a few hours. The alcohol and the cold facilitate the separation of the Potassium-bitartrate, which is slightly soluble in water but insoluble in alcohol. The liquid is then filtered, and heated to drive off the alcohol. This preparation contains some hypophosphorous acid, which, being a reducing agent, preserves the liquid from becoming yellow by oxidation.

2, By placing Phosphorus in water and gradually adding Iodine. The mixture is then distilled. The Phosphorus unites first with the Iodine, forming Phosphorus-iodide (PI_3 or PI_5, depending on the relative quantities of Phosphorus and Iodine present). The Phosphorus-iodide is decomposed by the water, forming hydriodic acid and an acid of Phosphorus (phosphorous or phosphoric acid):

$$PI_5 + 4H_2O = 5HI + H_3PO_4$$

3. By passing Hydrogen-sulphide through water containing Iodine-powder in suspension. The Iodine combines with the Hydrogen, the Sulphur precipitates:

$$H_2S + 2I = 2HI + S$$

Salts of hydriodic acid. These are called *iodides,* and are all colorless unless the metal colors them. Four salts should be remembered as colored: Silver-iodide, Lead-iodide, Mercurous-iodide and Mercuric-iodide. The first three are yellow, the fourth scarlet. Most iodides are soluble in water, but these four are not.

There are iodides besides those mentioned which are insoluble in water, but they are not important.

Tests for iodides: 1 Shaken with chloroform and a drop of Chlorine-water, they give a violet color to the chloroform; if Chlorine-water is in excess, the chloroform again gets colorless. 2, Silver-nitrate gives a yellow precipitate, insoluble in nitric acid and in ammonia water.

3, Differential test for bromides and iodides: add chloroform and drop of Chlorine-water; if iodides are present, the chloroform gets violet. If only bromides are present, the chloroform turns orange at once. If neither bromide nor iodide is present, the chloroform remains colorless. If both are present, the Iodine is indicated by the violet color; if a bromide is also present, the violet color disappears on the addition of an excess of Chlorine-water, and the orange color indicating a bromide is seen.

COMPOUND OF SULPHUR AND IODINE.

Sulphuris iodidum. According to the U. S. P., this is prepared by triturating flowers of Sulphur with Iodine, and heating the mixture first to 60° C., later to 100° C. The fused mass is then poured upon a porcelain plate. It appears as a grayish-black mass, having the odor of Iodine. It is insoluble in water, soluble in glycerine, Carbon-disulphide, etc. Alcohol, ether, or a solution of Potassium-iodide dissolves the Iodine, leaving the Sulphur. It has no definite chemical composition.

COMPOUNDS OF OXYGEN AND IODINE.

These are similar to those of Chlorine and Bromine.

Of the four hypothetical oxides of Iodine, only the pentoxide is known. Of the four theoretically possible acids, three are demonstrable:

HIO, hypo-iodous acid
HIO_3, iodic acid
HIO_4, periodic acid

FLUORINE.

SYMBOL, F; AT. MASS, 18.9; VALENCE, I.

Fluorine is a greenish-yellow or colorless gas of very irritating odor.

It is questionable if the smell is due to Fluorine itself, or if

it is caused by the hydrofluoric acid and ozone, as Fluorine decomposes water and forms these products.

It can be liquified by subjecting it to low temperature. At ordinary temperature it has great affinity for all other elements except Oxygen, with which it does not unite. Its action is so energetic that it readily dissolves metals, rocks, glass, porcelain, etc. Sulphur, Phosphorus, Iodine, Silicon, as well as many metals when in powdered form, take fire if brought into an atmosphere of Fluorine. Hydrogen explodes when it comes in contact with Fluorine. Organic substances like oil of turpentine, benzene, alcohol, cork, are inflamed by it. It decomposes water and forms hydrofluoric acid and oxygen:

$$H_2O + 2F = 2HF + O$$

In 1886 the French chemist Moissan discovered that at a very low temperature, liquified Fluorine loses its chemical activity, and no longer acts on glass, minerals, etc.

Preparation:

It is now prepared by passing an electric current through anhydrous hydrofluoric acid contained in Platinum vessels and maintained at a low temperature. As anhydrous hydrofluoric acid is a nonconductor of electricity, Sodium-fluoride is added. This renders the mixture a conductor. Hydrogen is formed at the negative, Fluorine at the positive pole.

Source:

Fluorine is found in certain minerals, especially fluorspar (Calcium-fluoride, CaF_2), and cryolite, which is a double salt of Sodium and Aluminum-fluorides.

$$AlF_3 + 3NaF$$

In the human body, it is contained in the enamel of the teeth, in the bones and in very small quantity in the blood.

History:

It was isolated by Moissan in 1886.

Hydrogen-fluoride (HF).

HYDROFLUORIC ACID (*acidum hydrofluoricum*) is a colorless, volatile liquid of irritating odor, boiling at 19.5° C. It produces very painful wounds if it comes in contact with the skin. It is soluble in water, the solution thus formed being colorless. It is an excellent solvent for glass and many minerals, and must be kept in rubber or paraffin vessels. It is used to etch glass, in assay work, etc. It dissolves all metals but Gold, Platinum and Lead; and vessels of these metals are used in its preparation.

Preparation:

By treating fluorspar with sulphuric acid:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

NITROGEN.

SYMBOL N; AT. MASS, 13.93; VALENCE, (I) III, V.

Physical properties:

Nitrogen is a colorless, odorless and tasteless gas, almost insoluble in water. It can be liquified by great pressure and low temperature, and forms a colorless liquid which boils at —194°C.

Source:

Nitrogen is found in a free state in the air, which is a mixture of about 79 percent Nitrogen and 21 percent Oxygen; further, combined with other elements in the protoplasm of animals and plants. All albuminous matter contains Nitrogen. It cannot be used in the elementary state in the metabolism of living organisms.

A few bacteria are able to build up higher Nitrogen compounds from the free Nitrogen of the air.

Animals need organic compounds of Nitrogen. Plants are able to take up inorganic Nitrogen compounds, like the nitrates and ammonium salts. The Nitrogen of the air is converted into these inorganic salts by the passage of electric sparks through the air (lightning). Nitrite of ammonium is formed,

and this settles on the ground and is used by the plants. Nitrite of ammonium is also formed in the air during oxidation and combustion. As animals are unable to assimilate inorganic Nitrogen compounds, they obtain the necessary Nitrogen from the flesh of other animals or from plants. Organic food which contains Nitrogen is called *nitrogenous food* or *proteid*. When organic substances decay, the Nitrogen compounds in them form ammonia, to which a part of the smell of putrifaction is due. By further decay and oxidation, the ammonia changes to nitrous acid and then nitric acid, and these form nitrates with the metals of the ground. Crystals of nitrates are often seen on the floors and walls of stables. The name 'Nitrogen' is derived from the word *niter* which was the name given to Potassium-nitrate (saltpeter).

Chemical properties:

Nitrogen does not burn nor support combustion. It is not a poison, although we cannot live in an atmosphere of pure Nitrogen because we need Oxygen. Its affinity for other elements is small, only a few, like Boron, Magnesium and Lithium, uniting with it directly when heated in a current of the gas. They form *nitrides*, as Mg_3N_2.

Preparation:

According to the source, we recognise two kinds of Nitrogen:
1. Atmospheric, prepared from air.
2. Chemical, made from chemical compounds containing it.

1. *Atmospheric Nitrogen.* (a). By burning Phosphorus under a glass bell which stands on a dish of water. The burning Phosphorus takes up Oxygen and forms oxide of Phosphorus, which dissolves in the water. The freed Nitrogen is left in the bell.

(b). By shaking air with an alkaline solution of pyrogallic acid, which absorbs the Oxygen and leaves the Nitrogen.

(c). By passing air through a heated tube containing metallic Copper; the Oxygen of the air being taken up by the Copper and Nitrogen left.

(d). By shaking air with a solution of Ferrous salt and

Potassium-hydroxide. The Ferrous-hydroxide precipitated takes up the Oxygen from the air, forming Ferric-hydroxide and leaving the Nitrogen. A Manganese salt is preferable to a Ferrous salt.

2. *Chemical Nitrogen.* (a). Pass Chlorine gas through ammonia.

$$NH_3 + 3Cl = 3HCl + N$$

(b). Heat ammonium-nitrite, which splits into water and Nitrogen:

$$NH_4NO_2 = 2H_2O + 2N$$

Instead of a solution of ammonium-nitrite, a solution containing ammonium-chloride and Sodium-nitrite may be employed.

In 1894 Lord Ramsey and Prof. Raleigh discovered the atmospheric Nitrogen to be somewhat heavier than the chemical Nitrogen, the atmospheric containing some heavy gaseous impurities, collectively called *argon.* Argon is a colorless, odorless and tasteless gas; it does not burn, nor is it a supporter of combustion . It does not unite with other bodies, hence its name, which means 'without energy'. Its molecule consists of one atom. It was further proven to be a mixture of six different elementary gases. The element contained in this mixture in the largest quantity retained the name *Argon,* the others being called *Metargon, Krypton, Xenon, Neon* and *Helium.* All are colorless odorless, tasteless and non-combustible gases. The element Neon is the only one which has not, as yet, been liquified. Helium, long before its discovery on our earth, was known to be present in the atmosphere of the sun. Helium is contained in some minerals.

Helium is contained in minerals which contain the rare metals Uranium, Thorium and Yttrium, as Cleveite, Uraninite, etc. It can be obtained by heating these with sulphuric acid.

History:

Nitrogen was discovered by Rutherford in 1772.

THE ATMOSPHERE.

The several constituents of the earth's atmosphere have been discussed under their respective headings. W will here briefly enumerate a few of the more important characteristics of the mixture.

The Atmosphere is a colorless, odorless, tasteless gas. One liter of it under ordinary conditions weighs 1.29276 grams (14.43 times as heavy as Hydrogen). It is a mixture of several constituents, the principal members being Oxygen and Nitrogen. It also contains water-vapor, Carbon-dioxide, ammonia, ozone, nitric acid (in the form of Ammonium-nitrate and Ammonium-nitrite), and the newly discovered gases of the Argon class.

Air is somewhat soluble in water, the Oxygen more so than the Nitrogen. If water is saturated with air, and this later driven out from the solution, the air will now be found to contain a larger amount of Oxygen. Attempts have been made to utilise this fact in the preparation of Oxygen.

Air can be liquified by cold and pressure. The critical temperature is —140° C. Liquid air is colorless and often turbid, on account of the undissolved Cabon-dioxide contained. It boils at —190° C., the Nitrogen evaporating in much larger proportion, while the Oxygen, which is less volatile, accumulates in the unevaporated residue. This fact may be applied to the preparation of Oxygen. Liquid air has a temperature of —190° Mercury, dipped in liquid air, solidifies; alcohol crystallises etc.

The principal proofs that air is a mixture and not a compound are:

1, The composition of air varies, while that of a chemical compound is always the same (*law of definite proportions*).

2, The weight-quantities of the elements in a compound bear a simple ratio to the atomic masses; this is not the case with air.

3, If the different components of air are artificially mixed in proper proportion, a mixture having all the properties of air is obtained. This process is not attended by changes of temperature or volume, which would occur were chemical action to take place.

4, Were air a compound, its aqueous solution should contain the same proportions of the elements of the air as exist in the atmosphere; while, in reality, a much larger proportion of Oxygen is dissolved from the air than of Nitrogen.

5, The components of air can be partially separated by simple physical operations, like diffusion (see atmolysis).

COMPOUNDS OF NITROGEN AND HYDROGEN.

There are several of these, but two are of great importance. The first of these is ammonia, NH_3; the second compound we should expect to be NH_5, but this is not known. Its radicle is known, however, in which one of the Hydrogen atoms of NH_5 is replaced. This radicle unites with Chlorine, Bromine, Iodine and other radicles, as NH_4Cl, $(NH_4)_2SO_4$, etc.

This radicle (NH_4), is the *ammonium radicle,* and has a valence of 1.

Ammonium, although it does not exist in the free state, behaves in its compounds like a metal, and unites with acids to form the ammonium salts. The physical and chemical properties of these are similar to those of Potassium and Sodium, their formulae also corresponding:

Chlorides: KCl; $NaCl$; NH_4Cl.
Nitrates: KNO_3; $NaNO_3$; NH_4NO_3.
Sulphates: K_2SO_4; Na_2SO_4 $(NH_4)_2SO_4$

Ammonium is considered as a metal; its salts will therefore be studied with those of Sodium and Potassium.

Ammonia, (NH_3).

AMMONIA is a colorless gas of irritating odor; it can be liquified by compression and cold, and the resultant liquid is colorless and readily boils when exposed to air. On evaporation, it produces such great reduction of temperature that it is used in ice machines. It is freely soluble in water, and two solutions are official: *Aqua ammoniae fortis* (28 percent) and *aqua ammoniae* (10 percent). These have the same odors as the gas, and on being boiled the ammonia is driven off. It is considered that ammonium-hydrate (NH_4OH) is contained in ammonia water:

$$NH_3 + H_2O = NH_4OH$$

Ammonia is also soluble in alcohol, and such solution is official as *spiritus ammoniae* (10 percent). It is made by heating strong ammonia water and passing the gas through alcohol, where it dissolves.

Ammonia has a strong alkaline reaction, and turns red litmus paper blue. It is called the *volatile alkali,* in contradistinction to the fixed hydroxides of Sodium and Potassium.

When treated with an acid, the Nitrogen in ammonia becomes 5-valent; one of the two additional valences is satisfied by the Hydrogen atom of the acid, the other by the radicle of the acid. This forms the ammonium salt:

$$N\begin{cases}-H\\-H\\-H\end{cases} + HNO_3 = N\begin{cases}-H\\-H\\-H\\-H\\-NO_3\end{cases} \text{ or } NH_4NO_3$$

Ammonia and nitric acid form Ammonium-nitrate.

As many molecules of ammonia are required for the formation of a neutral salt as there are replaceable Hydrogen atoms in the acid of the salt:

$$\begin{matrix}NH_3\\NH_3\end{matrix} + H_2SO_3 = \frac{NH_4}{NH_4}SO_4 \text{ or } (NH_4)_2SO_4$$

Two molecules of ammonia + sulphuric acid = ammonium-sulphate

Ammonia gas does not burn in air, but will burn in pure Oxygen. It is formed when organic matter decays. Ammonium-chloride was prepared by the Persians by the sublimation of camels' dung. It may be prepared by the destructive distillation of organic matter containing Nitrogen. Ammonia is contained in the gas liquor of gas works in large quantities. This is used for the preparation of ammonia water by heating it with lime and passing the gas into distilled water. Dry ammonia gas is best prepared by heating ammonium-chloride with powdered lime:

$$2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3$$

In addition to ammonia and the univalent radicle ammonium, Hydrogen and Nitrogen together form several other important compounds and radicles.

1. The AMIDO group (NH_2)—a univalent radicle obtained by removing one Hydrogen atom from the formula of ammonia. It does not exist in a free state, but its compounds occur frequently in organic chemistry and they are called the amido-compounds, amides, etc. The radicle replaces H or OH to form these compounds. For instance, with nitric acid it forms nitr-amide:

NO_2—OH, nitric acid
NO_2—NH_2, nitr-amide

2. The IMIDO group (NH)—a bi-valent group obtained by removing two atoms in the formula of ammonia. It does not exist in the free state, but as the imido-compounds; like the imide of sulphuric acid, (SO_2=NH), sulphimide, where NH replaces two OH groups.

3. HYDRAZINE or DIAMIDE—a compound of two amido groups:

(NH_2)—(NH_2)

of great importance in organic chemistry. It is a colorless liquid, and can be distilled. It fumes in air. It is a strong reducing agent, non-explosive but poisonous. It unites with acids and forms salts, the HYDRAZINE or DI-AMMONIUM SALTS.

By the action of acids, one or both of the Nitrogen atoms become 5-valent. There are two classes of hydrazine salts:

(a). The mon-acid salts—in which one Nitrogen atom is tri-valent, having two points of valence satisfied by Hydrogen atoms; the other Nitrogen is penta-valent, three points of valence being satisfied by Hydrogen atoms and the fourth by the acid radicle. The third valence of the trivalent Nitrogen is united with the fifth valence of the pentavalent Nitrogen atom:

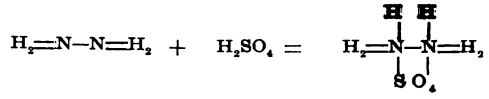
$$H_2{=}N{-}{-}N{=}H_2 + HNO_3 = H_2{=}N{-}{-}\overset{\overset{NO_2}{|}}{\underset{\underset{H}{|}}{N}}{=}H_2$$

Hydrazine and nitric acid form hydrazine-mono-nitrate

In these mon-acid salts of hydrazine, we assume the presence of a univalent radicle, N_2H_5. They are the most stable of the hydra-

zine compounds. This radicle also unites with OH and forms Hydrazine mono-hydrate, N_2H_5OH, a fuming, corrosive liquid which attacks glass, rubber, cork, etc., and must be prepared in Platinum vessels.

(b). The di-acid hydrazine salts, in which both Nitrogen atoms are 5-valent ,one valence of each being taken up by the other Nitrogen atom, leaving four valences of each free; of these three are taken up by Hydrogen atoms, the fourth by acid radicles:



In these di-acids, we assume the presence of the divalent group N_2H_4.

4. HYDRAZOIC ACID (azo-imide): The azo- compounds are considered as Nitrogen compounds containing two tri-valent Nitrogen atoms linked together by double bonds, leaving one valence of each free (—N=N—). Hence azo-imide is $N_2{=}NH$.

This is a colorless, mobile liquid, of an unbearable odor. It is explosive. In other respects it resembles hydrochloric acid. It is soluble in water, where it has an acid reaction, and unites with bases to form salts, the Hydrogen atom of the acid being replaced by atoms of metals. Sodium-hydrozoate is N_3Na.

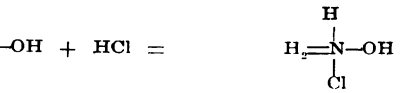
The salts of hydrozoic acid are called AZIDES or HYDRAZOATES; they contain the univalent radicle N_3.

5. AZIDE OF AMMONIUM: $NH_4{-}N_3$ or N_4H_4

6. MONAZIDE OF HYDRAZINE: $N_2H_5{-}N_3$ or N_5H_5

7. DI-AZIDE OF HYDRAZINE: $(N_2H_5){=}(N_3)_2$ or N_8H_6

8. HYDROXYLAMINE or OX-AMMONIA (NH_2OH) is ammonia in which one H atom is replaced by an OH group. It occurs as colorless, odorless needles, melting easily. It is unstable, and when quickly heated, often explodes. It absorbs moisture and is readily soluble in water, forming an alkaline solution. It unites with acids and forms the HYDROXYLAMINE SALTS:



Hydroxylamine and hydrochloric acid form hydroxyl-ammonium-chloride

OXYGEN COMPOUNDS OF NITROGEN.

Oxygen and Nitrogen form three regular compounds, explainable by the valence of Nitrogen; and three irregular compounds not apparently conforming to the valence of Nitrogen:

Regular:	*Irregular*:
N_2O, Nitrogen-monoxide.	NO, Nitric oxide.
N_2O_3, Nitrogen-trioxide.	NO_2, Nitrogen-oxide.
N_2O_5, Nitrogen-pentoxide.	N_2O_4, Nitrogen-tetroxide.

The latter compounds cannot be explained by valence, except the last one (see later).

Nitrogen-pentoxide (N_2O_5) appears in the form of white crystals, soluble in water with the generation of heat and the formation of nitric acid.

$$N_2O_5 + H_2O = H_2N_2O_6 \text{ or } 2HNO_3$$

Nitric acid (HNO_3)

NITRIC ACID (*acidum nitricum*), also called *aqua fortis,* is a colorless liquid of sharp smell which fumes in air. It sometimes turns yellow or brown when exposed to light, a part of it splitting and forming Nitrogen-dioxide, a brown gas which colors the acid. If a nitric acid weaker than 68 percent is distilled, it gives off steam until the residue has a strength of 68 percent, when an acid distils over of just this percentage undecomposed at 120.5° C. When an acid stronger than 68 percent is distilled, a portion is decomposed until the residue has a percentage of 68, and this then distils over undecomposed. It is official in two forms: Strong nitric acid, *acidum nitricum,* 68 percent; and dilute nitric acid, *acidum nitricum dilutum,* the strength of which is 10 percent.

Chemical properties:

(a). It is a strong oxidising agent, and is much used as such. When it oxidises, it usually splits up into water, nitric-oxide and Oxygen:

$$2HNO_3 = H_2O + 2NO + 3O$$

When mixed with hydrochloric acid, it forms water, Chlorine

and nitric-oxide, which latter unites with a part of the Chlorine, forming nitrosyl-chloride (NO.Cl).

$$2HNO_3 = H_2O + 2NO + 3O$$
$$3O + 6HCl = 3H_2O + 6Cl$$
$$2NO + 2Cl = 2NO.Cl$$

$$HNO_3 + 3HCl = 2H_2O + 2Cl + NO.Cl$$

added and cancelled.

When nitric acid is mixed with sulphurous acid, it changes the latter to sulphuric acid. Ferrous salts are converted by it into Ferric salts.

(b). Nitric acid is also an excellent solvent, all metals being dissolved by it except Gold and Platinum, which are not attacked at all, and Antimony and Tin, which are corroded to white powders(oxides of the metals).

(c). If nitric acid acts on organic substances, the Hydrogen atoms of the organic matter are removed and the univalent NO_2 radicle enters the compound. The products are the *nitro-compounds,* and are often very explosive. For instance, when nitric acid acts upon cotton ($C_6H_{10}O_5$), two or three atoms of Hydrogen are replaced by the same number of nitro-groups,

Di-nitro cotton $= C_6H_8.(NO_2)_2O_5$ or collodium cotton.
Tri-nitro cotton $= C_6H_7.(NO_2)_3O_5$ or gun-cotton.

Many of these nitro compounds are used as dyes.

Preparation. By distilling Potassium-nitrate with sulphuric acid. Potassium-sulphate and nitric acid are formed.
The nitric acid distils over.

$$2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3$$

It is advisable to use a large quantity of sulphuric acid. The tempera- required for the decomposition is then lower, and saving of nitric acid can be effected; the temperature not being high enough to decompose it. In such case, the bisulphate of Potassium is formed:

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$

Salts of nitric acid. These are called *nitrates,* and are colorless unless the metal colors them. They are all soluble in water.

Tests for nitric acid and nitrates. 1, add a few drops of an indigo solution which colors the solution blue; then a few drops of sulphuric acid; boil, and if nitric acid or nitrates are present, the solution is decolorised. 2, mix the solution to be tested with a solution of Ferrous-sulphate and carefully add sulphuric acid in such a way that it forms a layer on the bottom of the solution. A black zone where the two come in contact will be observed if nitric acid or nitrates are present. Instead of using a solution of Ferrous-sulphate, a small crystal of this salt may be put in the liquid to be tested and to which has previously been added some sulphuric acid. The crystal is coated black if nitric acid is present. 3, add to the solution to be tested a weak solution of brucine in water, then carefully underlay this with concentrated sulphuric acid. If nitric acid is present, a red ring is formed where the layers meet. 4, add to the solution to be tested a weak solution of diphenyl-amine, and carefully underlay with concentrated sulphuric acid. If nitric acid is present, a blue zone is formed where the layers meet.

Fuming Nitric Acid (Acidum Nitricum Fumans)

Fuming or red nitric acid is nitric acid in which a quantity of Nitrogen-dioxide is dissolved, giving to the solution an orange color and causing it to form brown fumes when exposed to air. It acts far more energetically than common nitric acid. If mixed with increasing quantities of water, it assumes first a green, then a blue color, and finally becomes colorless.

It is prepared: 1, By distilling a mixture of strong nitric and sulphuric acids. 2, By distilling a mixture of starch and saltpeter with sulphuric acid.

Nitro-hydrochloric Acid.

NITRO-HYDROCHLORIC ACID (*acidum nitro-hydrochloricum*), also called *nitro-muriatic acid* and *aqua regia,* is a mixture of nitric and hydrochloric acids. When these two acids are mixed, they effervesce and Chlorine escapes. The mixture contains water, free Chlorine and nitrosyl-chloride. Two forms are recognised by the U. S. P.: Strong *acidum nitro-hydrochloricum,* which consists of 180 parts of nitric acid and 820 parts of hydrochloric acid; and the diluted, *acidum nitro-hydrochloricum dilutum,* which contains 40 parts of nitric acid, 182 parts of hydrochloric acid and water sufficient to make 1000 parts. In making this preparation, the concentrated acids should first be mixed in a capacious vessel and, when all effervescence has ceased, transferred to amber colored bottles. If the diluted form is to be prepared, the dilution should be performed after the effervescence has ceased.

Nitro-hydrochloric acid will dissolve Gold and Platinum, forming chlorides of these metals.

Nitrogen-trioxide. (N_2O_3) is a bluish liquid of no particular importance. On being heated, it dissociates into NO_2 and NO.

$$N_2O_3 = NO_2 + NO$$

On cooling, the components again unite and form N_2O_3. Combined with water, it forms nitrous acid:

$$N_2O_3 + H_2O = 2HNO_2$$

It can be prepared by: 1, cooling a mixture of the gases NO and NO_2; the gaseous mixture condenses. 2, by distilling white Arsenic and nitric acid, and cooling the distillate in a freezing mixture.

Nitrous acid (HNO_2)

NITROUS ACID (*acidum nitrosum*), O=N—OH, is only known in diluted solution, where it is a colorless, unstable liquid.

It acts sometimes as a reducing, sometimes as an oxidising agent. As a reducing agent, it decolorises Potassium-permanganate, reduces chromic acid to green salts, etc. As an oxidising agent, it liberates Iodine from Potassium-iodide, bleaches indigo, etc.

The salts of nitrous acid are called *nitrites*. They are mostly soluble in water.

Preparation of nitrites. Heat the corresponding nitrate with metallic Lead or Copper, when the nitrite and Lead or Copper-oxide are formed:

$$NaNO_3 + Pb = NaNO_2 + PbO$$

Nitrogen-monoxide or *hyponitrous-oxide,* (N_2O), called also laughing gas, is a colorless gas of faint odor and sweetish taste. It can be liquified without great difficulty, forming a colorless, mobile liquid, which causes great cold on evaporation. It is somewhat soluble in water, and is collected over hot water, wherein it is less soluble. It is a supporter of combustion

Many substances, as Phosphorus, Sulphur, Carbon, burn in it with great brilliancy. The gas is first decomposed by the heat into Nitrogen and Oxygen, which latter supports combustion. When inhaled in diluted condition, it produces a sensation of exhilaration; hence the name. When inhaled in highly concentrated form it produces insensibility. This gas is used by surgeons and dentists and is called *vitalised air.* It is prepared by heating ammonium-nitrate, which splits into water and Nitrogen-monoxide:

$$NH_4NO_3 = 2H_2O + N_2O$$

Instead of using ammonium-nitrate, a mixture of Sodium-nitrate and ammonium-chloride may be used.

Nitric-oxide (NO) is a colorless gas insoluble in water. It is obtained by treating a metal, usually Copper, with nitric acid in the absence of air. In contact with air, it takes up Oxygen and forms brown Nitrogen-dioxide:

$$NO + O = NO_2$$

It dissolves in a solution of a Ferrous salt with a black color (used in the test for nitric acid). It can be liquified only with

great difficulty, and then forms a colorless liquid. Some substances are able to burn in the gas, which splits into Nitrogen and Oxygen. Other bodies do not burn because they do not develop sufficient heat to split the nitric-oxide.

On shaking nitric-oxide with Carbon-disulphide and then igniting the gas, a bright, quiet light is produced which contains many chemical rays and acts on photographic papers.

Nitrogen-dioxide, (NO_2) is a brownish, poisonous gas of pungent odor. It is obtained by mixing nitric-oxide with Oxygen:

$$NO + O = NO_2$$

or by treating a metal with nitric acid in the open air. It is a strong oxidising agent, and many substances burn in it.

Many metals (Copper, etc.) absorb large quantities of Nitrogen-dioxide at low temperatures, forming 'nitro-metals.'

Nitrogen-tetroxide (N_2O_4). This is a colorless liquid below 0°, and is obtained by cooling Nitrogen-dioxide ($N_2O_4 = 2NO_2$). It boils at 22°C,. the vapor becoming darker with increasing temperature, because it splits again into two molecules of NO_2.

In Nitrogen-tetroxide we assume that one of the Nitrogen atoms is tri-valent, the other penta-valent; and that they are linked together by an Oxygen atom, the free valence being also filled with Oxygen:

$$ON—O—NO_2 \text{ or } N_2O_4$$

This supposition is confirmed by the fact that cold water decomposes the compound into nitric and nitrous acids:

$$N_2O_4 + H_2O = HNO_2 + HNO_3$$

OTHER COMPOUNDS OF NITROGEN.

HYPONITROUS ACID (N—OH) of no importance.

NITROGEN and the HALOGENS.

These compounds are extremely explosive. Nitrogen is tri-valent in them.

1. NITROGEN-CHLORIDE (NCl_3) is an oily, yellow liquid, heavier than water. It is a very dangerous body, exploding with the most terrific effect by the most insignificant causes. It is prepared by treating ammonia-water or ammonium-chloride with an excess of Chlorine.

2. NITROGEN-BROMIDE (NBr_3) is a red, oily, very-explosive substance.

3. NITROGEN-IODIDE (NI_3). The substance known seems to be a compound of NI_3 and NH_3. It is obtained by treating powdered

Iodine with ammonia water. It is a brown powder and a very dangerous explosive.

Compound of the radicle NO: This is obtained by removing the OH group from nitrous acid, and is called nitrosyl. It is univalent. Its principal compound is NITROSYL-CHLORIDE (NO—Cl), a reddish-brown gas, which liquifies on cooling to a red liquid. It is formed when nitric-oxide (NO) is mixed with Chlorine. Also when nitric and hydrochloric acids are mixed.

Compounds of the radicle (NO_2): This univalent radicle is obtained by removing the OH group from nitric acid. It is called the NITROXYL or NITRO group. Of its inorganic compounds we may mention:

1. NITROXYL-CHLORIDE (NO_2Cl).

2. NITRO-SULPHONIC ACID (NO_2—SO_3H) can be considered as a compound of the nitro group with the univalent sulphonic acid group; or it may be considered as sulphuric acid in which one H is replaced by the nitrosyl group (HO—SO_2—O—NO). It is often formed in sulphuric acid factories in the Lead chambers when steam is not present in sufficient quantity, and its crystals are called the Lead-chamber crystals. It forms a crystalline, white, deliquescent mass: When water is added, it decomposes into sulphuric and nitrous acids.
It is formed when Sulphur-dioxide acts upon strong nitric acid:

$$SO_2 + HNO_3 = NO_2.SO_3H$$

Compounds of the radicle NH_2 are called AMIDO-COMPOUNDS

1. NITRAMIDE—a compound of the univalent nitro and amido groups (NO_2—NH_2).
2. AMIDO-SULPHONIC ACID (NH_2SO_3H).
3. SULPH-AMIDE: $OSO{=}(NH_2)_2$.
4. SULPH-IMIDE: $SO_2{=}NH$.

PHOSPHORUS.

SYMBOL, P; AT. MASS, 31; VALENCE, (I) III, V.

Phosphorus occurs in three different allotropic modifications: the ordinary yellow, the red or amorphous, and the black or metallic.

Source:

Phosphorus is found in nature in bones as Calcium-phosphate and in the nucleo-proteids of animals and plants. It was discovered in urine. It is found as phosphates in plants, and occurs in minerals, notably in apatite.

Yellow Phosphorus. This form appears as cylindrical sticks of transparent rolls of a garlic-like odor. It is soft and kneadable. It must be kept under water, wherein it is insoluble, for in air there is danger of self-ignition. It boils at about 287° C. At ordinary temperatures Phosphorus is volatile. It

is but slightly soluble in alcohol, more in chloroform and oils, and very freely in Carbon-disulphide. It is possible for it to be crystallised from its solution in Carbon-disulphide. It ignites by friction, and should be cut only under water. It is used for friction matches. In the dark, it gives off a greenish-white light—it is *phosphorescent,* and is very poisonous.

When Phosphorus burns in a sufficient quantity of air, Phosphorus-pentoxide is formed. The flame produced is very bright and hot, and in contact with the skin produces painful burns.

Red Phosphorus or *amorphous Phosphorus* occurs as a reddish-brown powder having properties almost diametrically opposite to those of the yellow modification. It is non-poisonous, insoluble in every known solvent, and does not ignite easily. It is used in the manufacture of the so-called 'Swedish matches.' If this form is heated to about 260° C., it changes into the ordinary Phosphorus.

Red phosphorus is prepared by heating the yellow in closed iron pots to about 240° C.

Metallic Phosphorus is of no importance.

Preparation:

Phosphorus is obtained by heating bones, the organic matter of which chars and turns black, forming *boneblack.* By further heating the bones turn white again, the Carbon being completely burned; this yields *bone-ash* (impure Calcium-phosphate). This is treated with sulphuric acid, and forms insoluble Calcium-sulphate and phosphoric acid (or, more correctly, mono-Calcium-phosphate). It is then filtered and the liquid mixed with Carbon, evaporated to dryness and distilled. The Phosphorus distils over, and is collected under water.

$$2H_3PO_4 + 5C = 3H_2O + 2P + 5CO$$

History:

Phosphorus was discovered by Brand in Hamburg and Kunkel in Wittenberg, 1670.

HYDROGEN COMPOUNDS OF PHOSPHORUS — PHOSPHINES.

There are three known:

1. *Gaseous Phosphine* (PH_3); also called *phosphoretted Hydrogen.* This gas is not spontaneously inflamable when pure, but is when prepared in the usual manner, because it contains liquid phosphine vapors. When gaseous phosphine burns, it forms water and the pentoxide of Phosphorus. It is evolved when Phosphorus is boiled with water and an alkali-hydrate. The hypophosphite of the metal used is also produced, and goes into solution:

$$3NaOH + 4P + 3H_2O = 3NaPO_2H_2 + PH_3$$

The gas obtained by this method is self-inflammable, because it contains liquid phosphine. In order to purify it, the gas is is passed through cooled tubes, where the liquid phosphine condenses. When purified in this manner it is not self-inflammable.

Phosphine has no action on litmus paper. Nevertheless it has some basic properties, although they are very weak. It unites with hydrochloric, hydrobromic and hydriodic acids, forming with them addition-products—just as ammonia does:

$$NH_3 + HI = NH_4I$$
$$PH_3 + HI = PH_4I$$

In these compounds we may assume the presence of the univalent radicle (PH_4) which is called *phosphonium;* its compounds are the *phosphonium compounds..*

PHOSPHONIUM-IODIDE (PH_4I) consists of colorless, shining crystals which can be sublimed. It fumes in air, and decomposes with water to form PH_3 and hydriodic acid. It may be prepared by passing phosphine gas and hydriodic acid gas into a flask immersed in a freezing mixture.

2. LIQUID PHOSPHINE ($H_2P—PH_2$) is analagous to hydrazine. It is a colorless, volatile liquid, spontaneously inflammable in air. If its vapors are mixed with other combustible gases like Hydrogen, it renders them self-inflammable. As its vapors are contained in the gaseous phosphine when prepared according to the usual method, the latter is self-inflammable.

3. SOLID PHOSPHINE, probably H—P=P—P=P—H, a yellow powder.

OXIDES OF PHOSPHORUS.

Phosphorus forms several oxides, the most important being the pentoxide, P_2O_5; also called phosphoric oxide. This is a

white, deliquescent powder, freely soluble in water—for which it has great affinity. It is one of the best dehydrating agents, and is much used as such. It is always formed when Phosphorus burns in a liberal supply of Oxygen. It combines with one, two and three molecules of water and forms three different acids:

$P_2O_5 + 3H_2O = 2H_3PO_4$, ortho-phosphoric acid.
$P_2O_5 + 2H_2O = H_4P_2O_7$, pyro-phosphoric acid.
$P_2O_5 + H_2O = 2HPO_3$, meta-phosphoric acid.

Orthophosphoric acid (H_3PO_4)

PHOSPHORIC ACID (*acidum phosphoricum*) is a thick, syrupy liquid of an agreeable sour taste, but no smell. It can also be obtained as colorless, hard, deliquescent crystals. It is a fixed substance, hence it cannot be distilled. When heated, it gives up water and forms pyrophosphoric acid:

$$2H_3PO_4 - H_2O = H_4P_2O_7$$

and when further heated, it gives up more water and forms metaphosphoric acid:

$$H_4P_2O_7 - H_2O = 2HPO_3$$

Orthophosphoric acid does not coagulate Albumen.

Orthophosphoric acid is official in two forms:

Acidum phosphoricum, 85 percent, and *acidum phosphoricum dilutum,* 10 percent.

Preparation of phosphoric acid. 1, By treating bone-ash with sulphuric acid. Insoluble Calcium-sulphate precipitates out, and phosphoric acid goes into solution. This is then filtered, and the filtrate evaporated to the desired percentage. Phosphoric acid prepared in this manner is not chemically pure, but contains Calcium; it is really primary Calcium-phosphate $Ca(H_2PO_4)_2$. It is not used for pharmaceutical purposes. 2, by treating Phosphorus with dilute nitric acid, which oxidises the Phosphorus to Phosphorus-pentoxide. This forms phosphoric acid with the water.

The salts of phosphoric acid are called *phosphates.* As phosphoric acid is tri-basic, it forms three series of salts:

(a). *Primary*—in which one Hydrogen atom is replaced by a metallic atom; as NaH_2PO_4.

(b). *Secondary*—in which two Hydrogen atoms are replaced by metallic atoms, like Na_2HPO_4.

(c). *Tertiary or neutral*—in which all three Hydrogen atoms are replaced by metallic atoms; as Na_3PO_4.

The neutral salts are all insoluble in water except those of the alkali-metals, Sodium, Potassium and Ammonium.

The common method of nomenclature does not specify to which of the three series the salt indicated belongs. The soluble phosphates of Na, K, NH_4, generally understood to be secondary salts (Sodium-phosphate is Na_2HPO_4). All other phosphates are understood to be tertiary salts (Calcium-phosphate is $Ca_3[PO_4]_2$).

The orthophosphates are usually colorless or white, unless the metal colors them. Silver-phosphate is yellow.

Tests for phosphoric acid and phosphates: 1, with Silver-nitrate they give a yellow precipitate, soluble in dilute nitric acid and also in ammonia. 2, with ammonia, ammonium-chloride and Magnesium-sulphate they give a white crystalline precipitate of Magnesium-ammonium-phosphate. 3, orthophosphoric acid does not coagulate albumin. 4, with nitric acid and ammonium-molybdenate they give a yellow precipitate when gently warmed.

Pyrophosphoric acid ($H_4P_2O_7$)

PYROPHOSPHORIC ACID (*acidum pyrophosphoricum*) is usually a colorless, syrupy, thick liquid of sour taste; but it can also be obtained in the crystalline state. It is prepared by heating the orthophosphoric acid. On solution in water, it slowly changes into orthophosphoric acid. Its salts, the *pyrophosphates*, are all insoluble in water, except those of Sodium, Potassium and ammonium. They are all colorless unles the metal colors them. Silver-pyrophosphate is also white.

Tests for pyrophosphoric acid and pyrophosphates: 1, with Silver-nitrate they give a white precipitate. 2, pyrophosphoric acid does not coagulate albumin.

Preparation. The pyrophosphates may be prepared by heating the secondary orthophosphates, when water is given up:

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$

Metaphosphoric acid (HPO_3)

METAPHOSPHORIC ACID (*acidum metaphosphoricum*) or, as it is commonly called, *glacial phosphoric acid,* appears in sticks or irregular lumps of a sour taste. It is deliquescent, and dissolves easily in water. Its solution changes slowly into orthophosphoric acid. It is prepared by heating orthophosphoric acid to 300° C., whereby it loses two molecules of water from its formula. The mass is then poured into moulds and cooled.

Pure metaphosphoric acid is really a soft, sticky mass The acid described here is the commercial one, which owes its hardness to the presence of some Calcium and Magnesium metaphosphates.

Its salts, the *metaphosphates,* may be obtained by heating the primary orthophosphates:

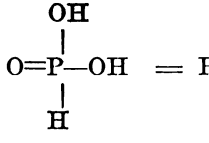
$$NaH_2PO_4 = NaPO_3 + H_2O$$

Tests for metaphosphoric acid and metaphosphates: 1, with Silver-nitrate they give a white precipitate. 2, metaphosphoric acid coagulates albumin.

Other acids of Phosphorus.

Besides the preceding three phosphoric acids, Phosphorus yields two others, the phosphorous and hypophosphorous acids. Their formulae can be derived from the orthophosphoric acid, as follows:

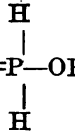
The formula of phosphorous acid is obtained by replacing one OH group in orthophosphoric acid by an atom of Hydrogen:



$= H_2PO_3H$, or phosphorous acid.

The formula of hypophosphorous acid is obtained by replac-

ing two of the OH groups of the orthophosphoric acid by atoms of Hydrogen:



$O{=}P{-}OH = HPO_2H_2$, or hypophosphorous acid.

Phosphorous acid (H_2PO_3H)

PHOSPHOROUS ACID (*acidum phosphorosum*) is a thick, sticky liquid, which may, however, become crystalline . It is decomposed by heat, forming orthophosphoric acid and gaseous phosphine. It is a reducing agent. In air it oxidises to orthophosphoric acid. It is best prepared by treating Phosphorous-trichloride with water:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

It is a dibasic acid, only two of the three Hydrogen atoms being replaceable by metallic atoms. Its salts are *phosphites*.

Hypophosphorous acid (HPO_2H_2)

HYPOPHOSPHOROUS ACID (*acidum hypophosphorosum*) is a thick syrupy liquid of sour taste; it may be crystallised. It is soluble in water. When heated it becomes more concentrated, but when the heat is sufficient it decomposes and forms self-inflammable phosphine and changes into orthophosphoric acid.

$$2H_3PO_2 = PH_3 + H_3PO_4$$

It is official in a 30 percent solution (*acidum hypophosphorosum*), and in a 10 percent solution (*acidum hypophosphorosum dilutum*). It is a strong reducing agent. For this reason it precipitates Gold and Silver from their solutions. It absorbs Oxygen from the air and changes to orthophosphoric acid. While this acid has three Hydrogen atoms, but one of them is replaceable by atoms of a metal—that of the OH group. It is therefore monobasic, and that is why the formula is written $HP\ O_2H_2$.

The salts of hypophosphorous acid, the *hypophosphites,* are nearly all soluble in water. The salts of the alkali- and alkali-

earth- metals are prepared by boiling the hydrates with Phosphorus and water. Phosphine (PH_3) is always evolved. The acid itself may be prepared by treating Calcium-hypophosphite or Barium-hypophosphite with sulphuric acid, forming an insoluble sulphate and hyposulphurous acid in solution. This is then evaporated to the desired strength. It is advisable to use oxalic acid in place of sulphuric acid when the Calcium salt is used.

AMIDO and CHLORINE COMPOUNDS of the PHOSPHORIC ACIDS.

By replacing OH groups in the phosphoric acids by Chlorine atoms or by amido-groups, the chloro-phosphoric acids and the amido-phosphoric acids are obtained

$PO.(OH)_3$, phosphoric acid.
$PO.(OH)_2.Cl$, mono-chloro-phosphoric acid.
$OP.OH.Cl_2$, di-chlor-phosphoric acid
$OP.Cl_3$, phosphoryl-chloride
$OP.(OH)_2.NH_2$, amido-phosphoric acid
$OP.(NH_2)_3$, phosphoryl-tri-amide

The pyro-phosphoric acid and the meta-phosphoric acid also form derivatives of this kind.

Of these compounds, only the phosphoryl-chloride is of importance. Its formula is $OP.Cl_3$, and it is also called Phosphorus-oxy-chloride. It is a heavy, colorless, volatile, fuming liquid, which can be distilled. It is one of the strongest dehydrating agents known, uniting with water with the generation of heat and forming ortho-phosphoric and hydrochloric acids.

If it acts upon substances containing the group OH, it withdraws this group and replaces it by Chlorine.

It is prepared by decomposing Phosphorus-pent[illegible] with a little water: $PCl_5 + H_2O = POCl_3 + 2HCl$.

Compounds are also known which are derived from the phosphoric acid by partly replacing the OH groups by Chlorine, partly by amido-groups.

COMPOUNDS of SULPHUR and PHOSPHORUS.

Several different ones may be prepared by heating Sulphur and Phosphorus together. Red Phosphorus is employed, to lessen the danger of explosion. Most of the sulphides of Phosphorus are crystalline solids which are decomposed into Hydrogen-sulphide and an acid of Phosphorus. The best known is P_2S_5.

THIO-PHOSPHORIC ACIDS are derived from the phosphoric acid by replacing part or all of the O atoms by S. Thio-phosphoric acid is H_3PS_4

COMPOUNDS OF PHOSPHORUS WITH CHLORINE.

Phosphorus, having a valence of 3 and 5, forms two chlorides:

PCl_3, Phosphorus-trichloride.
PCl_5, Phosphorus-pentachloride.

Phosphorus-trichloride (PCl_3) is a heavy, colorless, volatile liquid which fumes in air and boils without decomposition. It is decomposed by water, with the evolution of heat, forming hydrochloric and phosphorous acids:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

It is prepared by passing Chlorine gas over Phosphorus contained in a retort, which is gently heated. The Phosphorus unites with the Chlorine with the production of flame, and Phosphorus-trichloride distils.

Phosphorus-pentachloride (PCl_5) is a yellow-white solid appearing in crystalline form. It fumes in air, and sublimes without melting. On being heated it dissociates, forming Phosphorus-trichloride and free Chlorine—which latter can be recognised by the greenish color of the vapors. On being cooled, the two unite and again form PCl_5. With water, it forms phosphoric and hydrochloric acids:

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

It is prepared by passing Chlorine gas through Phosphorus-trichloride.

Both chlorides of Phosphorus are excellent dehydrating agents as they withdraw water from its compounds. They also withdraw the OH group from compounds containing it, and replace it by Cl. Phosphorous or phosphoric acid is formed. This reaction renders the chlorides of Phosphorus valuable in organic chemistry.

The compounds of Phosphorus with Bromine, Iodine and Fluorine are analagous to the Chlorine compounds, as PBr_3 and PBr_5. They are prepared by the direct contact of the elements.

ARSENIC.

SYMBOL, As; AT. MASS, 74.4; VALENCE, III, V.

Arsenic occurs in two allotropic modifications, crystalline and amorphous.

1. *Crystalline*: Arsenic has a metallic lustre, is gray and very brittle. On being heated, it evaporates without melting;

and the yellow vapors evolved have the smell of garlic. Arsenic can be sublimed. It is insoluble in water, alcohol, etc., but dissolves in acids. It is oxidised by nitric acid to arsenic acid. Arsenic is burnable, yielding a bluish flame; and this forms the trioxide (As_2O_3). Bromine and Chlorine readily unite with Arsenic. When powdered Arsenic is thrown into Chlorine, it ignites and forms Arsenic-trichloride. If Arsenic is poured into liquid Bromine, it also ignites, floating on the surface and burning there. Arsenic is used to harden shot.

2. *Amorphous.* This variety is prepared by passing Hydrogen-arsenide through heated tubes. It is very similar to the preceding, except that it is black in color and has a lower specific gravity.

Occurrence and preparation:

Arsenic is a very common element. It is found in nearly every mineral in small quantities, and there is hardly a chemical in which traces of it cannot be detected. It is found in combination with Sulphur as realgar and orpiment; and combined with various metals in the arsenic ores. These ores are roasted in furnaces, and the Arsenic burns and forms Arsenic-trioxide (As_2O_3). The later is volatile, and is led into cold rooms where it solidifies, forming a white powder, *white arsenic* or *flowers of Arsenic.* In order to prepare metallic Arsenic, the white Arsenic is mixed with Carbon and sublimed. The Carbon takes up the Oxygen and liberates the Arsenic, which sublimes:

$$As_2O_3 + 3C = 2As + 3CO$$

OXIDES OF ARSENIC.

Two oxides of Arsenic are known: Arsenous-oxide, As_2O_3, and Arsenic-oxide, As_2O_5.

Arsenic Trioxide.

Arsenous-oxide (*Arseni trioxidum*), also called arsenous acid (erroneously, as the real acid, though not known, would be, theoretically, formed by the addition of water), is a very poisonous substance. It exists in two forms, the crystalline or porcelain-like and the amorphous or glass-like.

(a). *The porcelain-like arsenous-oxide* is crystalline (octahedron), and looks like masses of porcelain. It should be kept in pharmacies and used in medicine in this condition. It usually comes on the market in powder form, and is called *white Arsenic.* It has no odor and but slight taste. On being heated, it volatilises without melting. It is quite heavy, but is sometimes seen to float on water, on account of its fatty surface, which does not allow it to become wet. It is only slowly soluble in water, and it takes a long time to make a saturated solution. Solutions can be made much more quickly by the addition of hydrochloric acid, an alkali, Sodium-bicarbonate, etc. Two such solutions are official: *liquor acidi arsenosi,* consisting of 1 percent white Arsenic, 5 percent dilute HCl, and the rest water; and *liquor Potassii arsenitis,* which contains 1 percent white Arsenic, 2 percent Potassium-bicarbonate, and the balance water. It is flavored and colored with tincture of lavender compound. It is commonly known as *Fowler's solution.*

(b). *The glass-like arsenous-oxide,* (arsenic glass), looks like glass and is amorphous . It is more soluble than the porcelain-like, and when a saturated solution of it is placed in a cold room, it crystallises in the porcelain-like form. If a hot saturated solution in hydrochloric acid is cooled and crystallization takes place in the dark, a kind of lightning is observed to occur in the liquid. The glass-like form gradually changes into the other, the change operating from the outside inwards. Pieces of porcelain-like arsenous-oxide are often met with which contain a core of the glass-like form.

With water, the Arsenic-trioxide forms three hypothetical acids:

$As_2O_3 + H_2O = 2HAsO_2$, met-arsenous acid.

$As_2O_3 + 2H_2O = H_4As_2O_5$, pyro-arsenous acid.

$As_2O_3 + 3H_2O = 2H_3AsO_3$, ortho-arsenous acid.

They cannot be obtained in isolated condition, but their salts, the *arsenites* are known. For instance, in Fowler's solution the met-acid is present, the formula of Potassium-arsenite being $KAsO_2$. Silver-arsenite has the formula Ag_3AsO_3, ortho-arsenous acid being present.

Arsenic-pentoxide (As_2O_5) appears as a white glasy solid. It is very soluble in water, forming the three arsenic acids:

$$As_2O_5 + H_2O = 2HAsO_3, \text{ met-arsenic acid.}$$
$$As_2O_5 + 2H_2O = H_4As_2O_7, \text{ pyro-arsenic acid.}$$
$$As_2O_5 + 3H_2O = 2H_3AsO_4, \text{ ortho-arsenic acid.}$$

They are analagous to the phosphoric acids.

Ortho-arsenic acid (H_3AsO_4)

ARSENIC ACID (*acidum ortho-arsenicum*) is the only one of the arsenic acids which is of importance. It closely resembles phosphoric acid, and is usually obtained as a thick, syrupy liquid, without odor, and of a sour taste. When evaporated, it yields colorless, deliquescent crystals. When heated, it changes into pyro-arsenic acid, and on further heating into the met-arsenic acid. It may be prepared by boiling white arsenic with nitric acid.

The salts of ortho-arsenic acid, the *arsenates,* are isomorphous with the ortho-phosphates; all are colorless unless the metal colors them—except Silver-ortho-arsenate, which is red. They are all insoluble in water, except those of the alkali-metals, Sodium, Potassium and Ammonium. The official soluble arsenates have only two Hydrogen atoms of the acid replaced, and are secondary salts. The official Sodium-ortho-arsenate is Na_2HAsO_4 The insoluble arsenates are tertiary salts and have all three atoms of Hydrogen replaced by atoms of the metal.

SULPHUR COMPOUNDS OF ARSENIC.

There are three of them:

Arsenic-trisulphide (As_2S_3) is a yellow powder or a brilliant yellow crystalline mass known as *auripigment* or *orpiment.* It is insoluble in water and diluted acids, but soluble in alkali-hydrates and in alkali-sulphide solutions. It is employed in paints, and is used to remove hair. It is found in nature, and can also be prepared by heating metallic Arsenic and Sulphur in the proper proportions. Another method of preparation

is to pass Hydrogen-sulphide through an acidulated solution of Arsenic.

Arsenic-penta-sulphide (As_3S_5) is also a yellow powder, and is very similar to the arsenic-trisulphide.

Arsenic-disulphide or *realgar* (As_2S_2 or S=As--As=S), occurs in beautiful ruby-red crystals. It is found in nature, and may be prepared artificially by heating Arsenic and Sulphur in proper proportions.

Just as the oxides of Arsenic unite with water and form the oxy-acids, so also do the sulphides of Arsenic theoretically unite with Hydrogen-sulphide (the Sulphur analogy of water) and form the sulpho-acids of Arsenic.

$$As_2S_3 + 3H_2S = \underset{\text{ortho-sulph-arsenic acid}}{2H_3AsS_4}$$

These sulpho-acids do not exist in a free state, but several of their salts are found in nature and can be prepared artificially. The alkali salts of these acids are soluble in water. The solubility of the Arsenic-sulphides in solutions of alkali-sulphides is thus explained.

OTHER COMPOUNDS OF ARSENIC.

Arsenous-chloride, Arsenic-trichloride ($AsCl_3$), is a colorless, oily liquid, fuming and very volatile. In contact with water, it splits into hydrochloric acid and Arsenic-trioxide.

$$2AsCl_3 + 3H_2O = 6HCl + As_2O_3$$

Arsenous-iodide, Arseni Iodidum (AsI_3), is official and comes on the market in red pieces having a faint odor of Iodine. It is prepared by heating Arsenic with an ethereal solution of Iodine in a flask fitted with a reflux condenser. It is somewhat soluble in water. When boiled with water, it splits into hydriodic acid and arsenous-oxide:

$$2AsI_3 + 3H_2O = As_2O_3 + 6HI$$

It enters into Donovan's solution (*liquor Arseni et Hydrargyri iodidi*).

Arsine, Hydrogen-arsenide or arsenuretted Hydrogen (AsH_3), is a colorless gas of bad odor and one of the most poisonous substances known. It burns with a bluish flame, and forms arsenous-oxide and water. When the flame is cooled by placing a cold porcelain plate in it, the Hydrogen alone burns and the Arsenic

is separated out, forming shiny black deposits on the plate. These spots are called the *arsenic mirrors*, and are soluble in a solution of chlorinated lime. If Hydrogen-arsenide is passed through a heated glass tube, it splits into Hydrogen and Arsenic; the Arsenic being deposited on the walls of the tube as a shiny black mirror.

When Hydrogen-arsenide is passed through a concentrated solution of Silver-nitrate, it forms a yellow precipitate; but when passed through a diluted solution of Silver-nitrate, it forms a black precipitate.

The yellow precipitate is a double compound of Silver-arsenide, Ag_3As, and Silver-nitrate: $AsH_3 + 6AgNO_3 = Ag_3As + 3AgNO_3 + 3HNO_3$
This yellow precipitate becomes black by the addition of water, metallic Silver, arsenous acid and nitric acid being formed.

$$(Ag_3As + 3AgNO_3) + 3H_2O = 6Ag + H_3AsO_3 + 3HNO_3$$

The black precipitate is therefore metallic Silver.

Hydrogen-arsenide is prepared by generating Hydrogen and introducing an oxide of Arsenic into the generating flask.

Small quantities of this extremely poisonous gas are formed when mould or other fungi or organisms act on compounds of Arsenic; this is why wall-paper containing Arsenic colors may be dangerous.
As Arsenic is a perfect analogy of Phosphorus, three arsines are to be expected, the gaseous, liquid and solid.
The solid arsine is a brown, velvet-like mass. The liquid arsine is not known, but some organic derivatives of it exist.

TESTS FOR ARSENIC.

1. Hydrogen-sulphide in acid solution gives a yellow precipitate.

2. Heated with coal, its compounds give up the smell of garlic.

3. When an Arsenic compound is heated in a narrow glass tube (Arsenic reduction tube) together with a small piece of charcoal, a black sublimate is formed on the cold walls of the tube.

4. *Marsh Arsenic test*: Hydrogen is generated in a flask by treating Zinc with sulphuric acid; the substance to be tested is also placed in the flask. The gas generated is led through a bent glass tube, at the mouth of which it is ignited. A cold piece of porcelain is placed in the flame and, if Arsenic is present, shiny black spots appear on the porcelain. Antimony compounds give similar mirrors, but they are dull black; further, the Antimony-mirror is insoluble in chlorinated lime.

5. *Gutzeit's test*: Put Zinc, sulphuric acid, and the substance to be tested in a test-tube and insert a plug of cotton dipped in Lead-acetate into the mouth of the tube. Place a few layers of filter-paper, previously dipped in a concentrated solution of Silver-nitrate, loosely over the mouth of the tube When Arsenic is present, Hydrogen-arsenide is evolved and turns the paper a yellow color, which becomes black on the addition of water. The cotton saturated with Lead-acetate serves to purify the arsenuretted Hydrogen of Hydrogen-sulphide and other substances which might affect the paper.

Modified Gutzeit's test (*U. S. P., 1900*): This test consists of two sections—(a) the preparation of the chemical to be tested, and (b), the test itself.

(a). The chemical is reduced by means of sulphurous acid. The solution to be tested is mixed with a very little sulphuric acid and a larger quantity of sulphurous acid, freshly prepared It is then evaporated down upon a water-bath.

(b). Metallic Zinc, dilute hydrochloric acid, and the substance to be tested are placed in a flask which has inserted into the lower end of its neck a wad of clean, dry gauze and above this some gauze impregnated with Lead-acetate solution. The mouth of the flask is closed by a cap of white filter-paper, upon the center of which a drop of a saturated alcoholic solution of Mercuric-chloride has been transferred and allowed to dry. Set the flask aside for a half-hour, then examine the inner side of the Mercuric-chloride test-cap—it will be yellow or orange if Arsenic is present. Antimony gives a dark gray or brownish-black coloration. If Sulphur compounds are present, the cap will be black, but so also will the Lead-acetate gauze.

6. *Bettendorf's test*: Put a solution of Stannous-chloride in strong hydrochloric acid and some of the substance to be tested into a test-tube; on gently heating this, a brown coloration or black precipitation will be obtained if Arsenic is present. This test is especially employed when compounds of Antimony are tested for Arsenic.

7. *Reinsch test*: Add to the solution to be tested some hydrochloric acid and a clean piece of Copper foil, and heat for several minutes. A grayish or black coating is deposited on the

foil. Take the foil from the liquid, and wash it in distilled water, dry without rubbing, and place in a reduction-tube. Heat the part of the tube containing the foil, and Arsenic mirrors are deposited on the cold portions of the tube if Arsenic is present.

ANTIMONY (Stibium).

SYMBOL, Sb; AT. MASS, 119.3; VALENCE, III, V.

Antimony closely resembles the metals. It is of a bright, bluish-white color, and is very brittle. It has crystalline structure. Only strong acids are able to dissolve it—nitric acid does not dissolve, but acts very energetically upon it and converts it into a white powder, an oxide of Antimony.

Antimony melts easily, and when the molten metal solidifies, it expands. Its alloys possess this same property of expansion, and this renders them suitable for fine, sharp castings.

Antimony burns with a bright flame, forming white vapors of Antimony-trioxide Sb_2O_3.

Occurrence:

It is found in nature in combination with Oxygen (*white Antimony, Antimony ochre*), and as Antimony-trisulphide (Sb_2S_3) which is called *stibnite* or *black Antimony*.

Preparation:

1. By heating Antimony-trisulphide with metallic Iron. The Iron takes up the Sulphur and forms Iron-sulphide, and Antimony is freed:

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb$$

2. By roasting Antimony-trisulphide. The Sulphur escapes as SO_2, and the Antimony is converted into an oxide. This is mixed with charcoal and heated. The Carbon combines with the Oxygen and forms CO_2 which escapes, and the metallic Antimony is left.

Antimony is employed in many alloys, as in type metal, Britannia metal, etc.

COMPOUNDS OF SULPHUR AND ANTIMONY.

As Antimony has a valence of 3 and 5, it forms two sulphides:

Antimony-trisulphide (*Antimonii sulphidum*) Sb_2S_3, commonly called *black Antimony,* is a grayish-black, heavy powder, insoluble in water and alcohol but soluble in hydrochloric acid with the evolution of Hydrogen-sulphide. It is crystalline. When Antimony-trisulphide is artificially prepared by passing Hydrogen-sulphide through an acid solution of Antimony, it appears as an amorphous, brick-red powder. If this is heated in Carbon-dioxide or treated with dilute hydrochloric acid, it changes to the black crystalline form.

Antimony-pentasulphide, (Sb_2S_5), sometimes called *golden Sulphur,* is an orange-red powder, insoluble in water, alcohol and ether. When heated , it decomposes into the trisulphide and free Sulphur. It dissolves in strong hydrochloric acid with the evolution of Hydrogen-sulphide. The Pharmacopoeiae of some countries recognise it, but not that of the United States. It is best prepared by boiling Antimony-trisulphide with Sulphur and a solution of Sodium-hydrate, and crystallising the resulting liquid. Yellow crystals are obtained, which consist of Sodium-ortho-sulph-antimonate, Na_3SbS_4, known as Schlippe's salt. These crystals are dissolved in water and hydrochloric acid added to the solution. There is a generation of Hydrogen-sulphide, and an orange precipitate of Antimony-pentasulphide results.

Both sulphides of Antimony may be regarded as acid sulphides which form with Hydrogen-sulphide the theoretical sulpho-acids as ortho-sulph-antimonic acid. $Sb_2S_5 + 3H_2 = 2H_3SbS_4$.

These acids are unknown in a free state, but some of their salts are of common occurrence. For instance, Schlippe's salt, Na_3SbS_4

The acid character of the sulphides of Antimony supplies a reason for the fact that they are soluble in solutions of alkalies and in solutions of sulphides of the alkali-metals. Of the sulph-antimonates, only the ortho- compounds are known; while all the classes of sulph-antimonites are known.

COMPOUNDS OF CHLORINE AND ANTIMONY.

Antimony, being 3- and 5-valent, forms two chlorides:

Antimony-trichloride, ($SbCl_3$), known as *butter of Antimony,* is a colorless, deliquescent, crystalline substance of the consistency of butter. It melts when warmed, and when sufficiently

heated can be distilled. It dissolves in dilute hydrochloric acid. If treated with a large quantity of water, it forms a white precipitate of Antimony-oxychloride (O=Sb—Cl), called *powder of algaroth*:

$$SbCl_3 + H_2O = SbOCl + 2HCl$$

The butter of Antimony found in pharmacies is crude Antimony-trichloride dissolved in hydrochloric acid. The orange color is due to some Ferric-chloride it contains. It is prepared by treating black Antimony with hydrochloric acid

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

Antimony-pentachloride ($SbCl_5$) is a yellowish liquid which is dissociated by heat into the trichloride and free Chlorine. It fumes in air. It is decomposed by water, forming antimonic acid. It is obtained by passing Chlorine gas through Antimony-trichloride.

OXIDES OF ANTIMONY.

Antimony forms two oxides:

Antimony-trioxide (Sb_2O_3) is a white, heavy powder. It can be sublimed, and then crystallises in two different forms—it is dimorphous. It is insoluble in water, alcohol, ether, nitric acid, but soluble in strong hydrochloric acid and freely soluble in a solution of tartaric acid. Digesting with cream of tartar and water will also dissolve it, yielding tartar emetic in solution. It is also soluble in solutions of Sodium- and Potassium-hydroxides.

Preparation. 1, by treating metallic Antimony with nitric acid. 2, by adding water to Antimony-trichloride; washing the precipitate produced (SbOCl) with ammonia or Sodium-carbonate to free it from Chlorine:

$$2SbOCl + 2NH_4OH = Sb_2O_3 + 2NH_4Cl + H_2O$$

The trioxide of Antimony has sometimes acid, sometimes basic properties—the latter predominate, however. The solubility of the oxide in solutions of Potassium-hydroxide or Sodium-hydroxide to form salts are evidence of acid properties, although these are weak. The salts thus formed are unstable. The basic properties of the oxide of Antimony are much more marked. It dissolves in acids (sulphuric, tartaric, etc.), forming two classes of salts:

(a). The regular Antimony salts—formed by replacing the Hydrogen

atoms of the acid by tri-valent Antimony atoms, as Antimony-sulphate $Sb_2(SO_4)_3$.

(b). The Antimonyl salts—formed by replacing the Hydrogen atoms of an acid by the univalent radicle (SbO), called stibyl or antimonyl. Antimonyl-nitrate is $(SbO)(NO_3)$.

Antimony-pentoxide (Sb_2O_5) is a straw-colored powder insoluble in water. It has acid properties, and unites with alkali metals and forms salts in which we assume the presence of the antimonic acids:

$$Sb_2O_5 + 3H_2O = 2H_3SbO_4, \text{ orth-antimonic acid.}$$
$$Sb_2O_5 + 2H_2O = H_4Sb_2O_7, \text{ pyro-antimonic acid.}$$
$$Sb_2O_5 + H_2O = 2HSbO_3, \text{ met-antimonic acid.}$$

They are of no particular importance and are not official. One of their salts, Potassium-pyro-antimonate ($K_2H_2Sb_2O_7$), is used as a Sodium test, as it forms the only Sodium salt that is insoluble in water.

COMPOUND of ANTIMONY with HYDROGEN.

Hydrogen-antimonide (SbH_3), also called antimonetted Hydrogen and stibine. It is a colorles gas of disagreeable odor; very poisonous, and resembling in its properties arsine. It burns, forming water and Antimony-trioxide. When the flame is cooled by holding a porcelain dish in it, it deposits black stains of metallic Antimony. These stains are insoluble in chloride of lime solution (differentiation from Arsenic). If the gas is passed through a heated glass tube, it is decomposed into Hydrogen and Antimony, which latter is deposited as black stains. It is made by generating Hydrogen by the action of sulphuric acid upon Zinc, and then adding a soluble Antimony compound to the reacting substances.

Tests for Antimony. In acid solutions, Hydrogen-sulphide gives an orange-red precipitate, which is soluble in ammonium-sulphide.

The elements Nitrogen, Phosphorus, Arsenic and Antimony form a natural class of elements. This class has a valence of 3 and 5, and is called the Nitrogen class or Phosphorus class.

VANADIUM, COLUMBIUM, TANTALUM .

The elements Vanadium, Columbium (or Niobium), and Tantalum are also closely related to the Phosphorus group, but have a more metallic character. Their valence is also 3 and 5, but more commonly 5. They form analagous compounds.

These elements are of little importance and of rare occurrenec.

Bismuth is a remote member of the Phosphorus group, it valence being 3 and 5, but more commonly 3. As it is metallic in character, it will be treated of with the metals.

CARBON.

SYMBOL, C; AT. MASS, 11.91; VALENCE, IV.

Carbon occurs in three allotropic modifications:

(a). *The diamond*—crystallised, colorless, glass-like and transparent, sometimes colored by impurities. It has great light-refracting power, and is the hardest substance known. Impure diamonds are therefore used for cutting glass and other resistant bodies. The diamond is absolutely insoluble in all known solvents; it is, however, combustible and burns in Oxygen, though having a far higher ignition temperature than is required to burn coal. It forms the same combustion-product that coal does, Carbon-dioxide (CO_2). The diamond is mined chiefly in South Africa and Brazil. Very small ones have been prepared artificially.

Molten Iron dissolves coal. When this solution is quickly cooled, the exterior portions, as they solidify, contract and exert great pressure upon the inner portions, where the Carbon crystallises as diamonds. Molten olivine, a mineral, also dissolves Carbon in the same manner.

(b). *Graphite*, also called *plumbago and black lead*, is found crystalline too. It is a dark-colored substance of metallic lustre, absolutely insoluble, and is very soft, smooth and soap-like to the touch. It is much used for lubricating purposes, for making lead-pencils (it leaves black Carbon on the paper), and many other purposes. It does not melt, but burns in Oxygen to CO_2. Its ignition-temperature is so high, however, that it is used in the manufacture of crucibles and other articles that are required to stand great heat. It is a good conductor of electricity and heat. California, Liberia and Ceylon are the chief sources.

When coal is dissolved in molten Iron and the molten metal slowly cooled, the Carbon crystallises in the form of graphite.

(c). *Coal* is a black, amorphous body insoluble in water, alcohol, ether and all ordinary solvents, but somewhat soluble in molten Iron; from which solution it usually crystallises in the graphite form. When boiled with sulphuric acid or nitric acid, it is converted into Carbon-dioxide (CO_2) and escapes as a gas. It is readily burnable, forming Carbon-dioxide when the supply of Oxygen is sufficient but Carbon-monoxide (CO) when burned in an insufficient quantity of Oxygen for its complete combustion. If heated with the oxides of the heavy metals, it

with-draws the Oxygen from them, forming Carbon-monoxide or Carbon-dioxide and the free metal.

This form of reduction is extensively employed in the mining industry to obtain metals from their ores, many of which are oxides.

There are two kinds of coal:

I. *Natural coal*—soft or bituminous, and hard coal or anthracite.

II. *Artificial coal*—obtained by heating organic substances without sufficient Oxygen for their combustion. There are several kinds of artificial coal:

(i). *Wood charcoal* (*carbo ligni*) made by heating wood in kilns without sufficient Oxygen to burn it. This variety absorbs large quantities of gas, especially of those gases which can be easily liquified, like Hydrogen-sulphide and ammonia. It is therefore used as a deodoriser. It also freely absorbs Oxygen, which is thus firmly compressed into its pores, and may ignite by the compression. This Oxygen is gradually given up to bodies which have affinity for it. Being thus an oxidising agent, coal is antiseptic and disinfectant—water may be purified by filtration through charcoal. Meat is often shipped packed in charcoal, the antiseptic powers of which keep it fresh. In medicine charcoal is used as an antiseptic and disinfectant, and is found in many tooth-powders.

(ii). *Animal charcoal* (*carbo animalis*) or *boneblack* is prepared by heating animal matter until it is charred. It contains only 10 to 12 percent of Carbon, but much Calcium-phosphate (derived from the bones). It is principally used for the decolorisation of liquids. Red wine is rendered colorless by it. It is much used in sugar factories. It is purified by treating it with dilute hydrochloric acid, and is then official as purified charcoal (*carbo animalis purificatus*).

(iii). *Lampblack* or *soot*. This is prepared by burning organic substances rich in Carbon, like turpentine, camphor, resins, and tar. These burn with a smoky flame which deposits lampblack.

(iv). *Coke* is obtained by heating brown coal or bituminous coal in retorts in the absence of Oxygen. Bituminous coal con-

tains Hydrogen, Nitrogen and some other elements, as well as Carbon. In the manufacture of coke, four important products are obtained: coke, which remains in the retort; coal-tar, which distils into receivers; gasliquor, which also distils and collects above the tar in the receivers; and gas, which is used for purposes of illumination. The process is the *destructive distillation of coal.* The by-product, coal-tar, is used extensively for the preparation of the coal-tar products (carbolic acid is a coal-tar product). The gas liquor has an alkaline reaction and contains ammonia.

(v). *Gas carbon.* During the destructive distillation of bituminous coal, a hard lining is formed on the walls of the retorts; this is called *Gas Carbon.* It is a very pure Carbon, and a good conductor of electricity. It is used for the Carbon poles in electric arc-lights and in electric batteries.

Sources of Carbon:

Carbon is contained in all substances derived from animals or plants. As carbon is contained in all organic substances, organic chemistry is the chemistry of Carbon and its compounds. Carbon is found in many minerals, usually as carbonates (chalk and marble are Calcium-carbonate). It is also found in combination with hydrogen as petroleum and asphalt.

OXIDES OF CARBON.

There are two oxides of Carbon: the regular, Carbon-dioxide (CO_2), and the irregular, Carbon-monoxide (CO).

Carbon-dioxide (CO_2) also called *carbonic acid gas,* is a heavy, colorless gas, which sinks in air and forms an invisible layer on the ground. It has a somewhat sour and sickening smell. It can be liquified by cooling and compression and has a critical temperature of 31.9° C. Liquid Carbon-dioxide is a colorless, mobile liquid, which does not mix with water, but floats upon it. It has a boiling point of —78° C. When exposed, a part of it evaporates rapidly, drawing heat from the portion not yet evaporated which becomes so cold that it solidifies. The solid Carbon-dioxide looks like snow; it is so cold that when

pressed upon the skin, it produces the same effect as hot Iron. The solid form evaporates without liquifaction.

Liquid Carbon-dioxide is brought on the market in drums, and is used very extensively in industry. The solid form is also much used.

Carbon-dioxide is poisonous, but is not nearly so baneful in its effects as the monoxide. It is somewhat soluble in water, one liter of water dissolves about one liter of the gas at ordinary pressure. Water charged with Carbon-dioxide under pressure is *carbonised water;* if the pressure is removed, it effervesces. CO_2 is not a poison in the stomach, but an agreeable stimulant. It does not burn, nor does it support combustion, and is used as a fire-extinguisher.

A suspected atmosphere may be tested for it by introducing a lighted candle: this will go out if a large amount of Carbon-dioxide is present.

Carbon-dioxide gives a precipitate of Calcium-carbonate when passed through a Calcium-hydroxide solution (limewater).

Carbon-dioxide is a constant constituent of the air in small quantities. Its presence there is due to the respiration of animals and other combustion processes. The oppressive feeling sometimes experienced in large assemblages is due to this gas. It would increase in the air were it not for the fact that the plants take it up and, under the influence of light, convert it into Oxygen, which they exhale, and Carbon, which they unite with water to form starch by their metabolism.

Carbon-dioxide emanates continually from the ground, especially in volcanic countries, some places being particularly rich in it—as, for instance, the dog cave in Italy . It is also frequently met with in considerable quantities in wells, springs, cellars, and other enclosed places.

It is also formed by the process of fermentation.

Preparation of Carbon-dioxide: 1, by burning coal
2, by the fermentation of sugar.
3, by treating a carbonate with an acid. True carbonic acid (H_2CO_3) is formed, but this, being unstable, breaks down:

$$H_2CO_3 = H_2O + CO_2$$

4, by heating an insoluble carbonate. This splits into the oxide of the metal and free Carbon-dioxide:

$$CaCO_3 = CaO + CO_2$$

The process of thus driving out the Carbon-dioxide from a carbonate is called *calcination.*

Carbonic acid (H_2CO_3).

CARBONIC ACID (*acidum carbonicum*) is not known in the free state, as it instantly breaks down into Carbon-dioxide and water. The salts, however, are known and are called *carbonates.* They are all colorless, unless the metal colors them. All are insoluble in water except those of the alkali-metals. The insoluble carbonates dissolve to a certain extent in water containing Carbon-dioxide, forming bicarbonates. Carbonic acid is a very weak acid, and if a carbonate is treated with another acid, carbonic acid is freed; being unstable, it splits into water and Carbon-dioxide, and the latter causes effervescence by its escape (this furnishes a test for carbonates).

Two radicles may be obtained from carbonic acid, by removing one or both OH groups:

—CO—OH (mono-valent) carboxyl
—CO— (divalent) carbonyl

Both of these unite with other radicles and form compounds.

Cl—CO—OH, Chloro-carbonic acid. (carboxyl-chloride)
CH_3—CO—OH acetic acid
Cl—CO—Cl, carbonyl-chloride (phosgene).

Carbon-monoxide (*CO*) is a colorless, odorless and tasteless gas, insoluble in water. It burns with a bluish flame, forming Carbon-dioxide. It can be condensed with difficulty. It is extremely poisonous, causing the so-called *coal gas poisoning.* It is formed in stoves where the supply of air is insufficient for complete combustion, and is also contained in illuminating gas (6 to 40 percent).

The poisonous action of Carbon-monoxide is due to the fact that it forms a compound with the hæmogobin of the blood. This compound is called *carboxy-haemoglobin* or *Carbon-monoxide haemoglobin,* and makes the blood unfit to fulfil its

normal function of carrying Oxygen. It may be detected by the spectroscope.

Carbon-monoxide is a strong reducing agent. It reduces the metals when passed over their heated oxides. It also reduces solutions of some of the precious metals, like Gold and Platinum, when passed through them—the metals being precipitated. A paper moistened with chloride of Palladium is blackened by it (this is a very delicate test). Carbon-monoxide is soluble in a solution of Cuprous-chloride.

Carbon-monoxide has the property of uniting with certain metals when passed over them in finely-divided state. The most remarkable of the resulting compounds is the Nickel-carbonyl, $Ni(CO)_4$, which is a colorless, mobile, highly refractile liquid, very volatile and combustible.

Preparation of Carbon-monoxide: 1, by burning Carbon in an insufficient supply of Oxygen. The blue flames sometimes seen in coalstoves are due to its presence. 2, by passing Carbon-dioxide over hot coal:

$$CO_2 + C = 2CO$$

3, by treating oxalic acid ($H_2C_2O_4$) with concentrated sulphuric acid. The oxalic acid splits up into water, Carbon-dioxide and Carbon-monoxide:

$$H_2C_2O_4 = H_2O + CO_2 + CO$$

The gases are then passed through Calcium-hydroxide, which absorbs the Carbon-dioxide.

COMPOUND OF CARBON WITH SULPHUR.

Carbon-disulphide (*Carbonei disulphidum*) is a colorless liquid of disagreeable garlic-like odor, heavier than water. It does not dissolve in water to any considerable extent, but sinks down in it. It is a great refractor of light. It is easily volatilised—even at ordinary temperature; and its boiling point is very low (46°C.). It is very combustible and burns with a blue flame, forming Carbon-dioxide and Sulphur-dioxide. It is an excellent solvent for fats, oils, resins, Sulphur, Phosphorus, Iodine, Bromine, rubber, etc., and is used in industry for removing fat from sheeps-wool, extracting oils from seeds, for preparing rubber cement and a hundred other useful purposes. Its vapors, when mixed with air, are very explosive.

It is prepared by heating coal and passing Sulphur vapors

over it. The resultant vapors of Carbon-disulphide are then liquified by cooling.

Carbon-disulphide may be considered as an acid sulphide with which H_2S forms the SULPHO-CARBONIC or THIO-CARBONIC ACID (H_2CS_3). The salts are called sulpho-carbonates or thio-carbonates, and are formed by dissolving Carbon-disulphide in solutions of the alkali-sulphides. The free thio-carbonic acid can be obtained by treating these salts with hydrochloric acid. It is a reddish-brown oil.

CARBON-OXY-SULPHIDE or CARBONYL-SULPHIDE (OCS) is also known. It is a colorless gas of offensive odor.

COMPOUNDS OF CARBON WITH NITROGEN, HYDROGEN AND HALOGENS.

The Nitrogen compounds of Carbon are of great importance and their study forms a branch of organic chemistry. They are compounds or the univalent radicle cyanogen(CN). This unites with other radicles, forming the cyanogen compounds, like H—(CN), which is prussic acid.

Hydrogen and Carbon unite to form an infinite number of compounds, one of the simplest being methane (CH_4), the common marsh-gas. They are called the hydro-carbons. They are of primary importance, and a knowledge of them is indispensable to the understanding of organic chemistry.

By replacing the Hydrogen atoms in the hydrocarbons by Chlorine, Fluorine, Bromine and Iodine, the halogen compounds of Carbon are obtained.

SILICON.

SYMBOL, Si; AT. MASS, 28.2; VALENCE, IV.

Occurrence and preparation:

Silicon is an element of very frequent occurrence. It is a constant constituent of rocks and minerals. The element itself is prepared in various ways, the simplest being by igniting a mixture of Silicon-oxide and Magnesium:

$$SiO_2 + 2Mg = 2MgO + Si$$

Silicon occurs in two allotropic modifications:

I. *Amorphous Silicon*, a dark brown powder, insoluble in

water and all acids, except hydrofluoric. It burns in air, forming Silicon-dioxide (SO_2).

II. *Crystalline Silicon,* a brilliant, steel-gray crystalline substance, insoluble in water and all acids except in a mixture of hydrofluoric and nitric acids. It does not burn in air or in Oxygen, even when strongly heated. Neither modification is of importance.

Silicon-oxide (SiO_2) appears in nature as sand and quartz and is prepared artificially, when it is a white powder and is called *silica.* This is sometimes used in pharmacy for making pills of substances like Silver-nitrate, which would decompose were organic substances used as excipients. Silica is insoluble in water and all acids except hydrofluoric; but dissolves in alkalies. When melted with large quantities of Sodium-carbonate, the molten mass will dissolve in water—which is found to contain Sodium-silicate. This solution is used in medicine for dressings instead of plaster of Paris, a it solidifies when exposed o air. It is also used for cementing porcelain and glass ware. It is called *liquid glass,* and is a thick, syrupy liquid, of strong alkaline taste and reaction. If an acid be added to the solution, a jelly-like precipitate of silicic acid (H_2SiO_3) is obtained.

If the silicic acid is filtered off, washed, dried and heated, it gradually loses its water and changes into the Silicon-oxide (SiO_2). The jelly-like acid is soluble in an excess of hydrochloric acid, and the solution is known as *colloidal silicic acid.* The formula may be illustrated as

$$SiO_2 + 2H_2O = H_4SiO_4$$

It is best prepared by adding liquid glass to an excess of hydrochloric acid. Sodium-chloride and colloidal silicic acid in solution are formed. They are separated by dialysis—the Sodium-chloride being a crystalloid, and the silicic acid a colloid.

In addition to the ones mentioned, there are many other silicic acids, formed by the addition of varying amounts of water to the oxide. They are *poly-silicic acids.*

$$2SiO_2 + 3H_2O = H_6\ Si_2O_7$$

They have the general formula:

$$m\,SiO_2 + n\,H_2O$$

Many of the minerals are compounds of these different acids with metals. These salts are *silicates*. Nearly all are insoluble in water, except those containing a large amount of Sodium or Potassium. Among the more important are:

Glass is a silicate of Sodium, Potassium, Calcium or Lead, and is manufactured by melting sand together with Potassium-carbonate, Sodium-carbonate, Lead-oxide or Calcium-oxide.

Clay is silicate of Aluminum and is found in deposits. It is used for the manufacture of earthenware. *Kaolin* is a fine grade of clay from which porcelain is made.

HYDROGEN-SILICIDE or SILICON-HYDRIDE (SiH_4) is a colorless gas. As obtained by the usual methods, it is spontaneously inflammable. The pure gas does not do so, but will, however, ignite when slightly warmed, if diluted with Hydrogen or the pressure is reduced.

SILICON-CHLORIDE ($SiCl_4$) is a colorless liquid, fuming in air. It decomposes on the addition of water into silicic and hydrochloric acids. It is prepared by heating Silicon in a stream of Chlorine.

SILICON-FLUORIDE (SiF_4) is a colorless, fuming gas of penetrating odor. It is obtained by treating a Silicon compound with hydrofluoric acid.

It is best prepared by mixing sand and fluorspar (CaF_2), anl treating this mixture with sulphuric acid. If the gas is passed through water, gelatinous silicic acid is precipitated, whilst an acid of the formula H_2SiF_6 goes into solution. This is called hydrofluo-silicic acid.

It may be considered as a compound of Silicon-fluoride with two molecules of hydrofluoric acid: $SiF_4 + 2HF = H_2SiF_6$.

Hydrofluo-silicic acid is only known in aqueous solutions; it is then a colorless liquid. of strong acid reaction and taste, which dissolves metals and bases to form the silico-fluorides. As its Potassium and Barium salts are insoluble, it may be used as a test for these metals.

SILICON-CARBIDE (SiC) also called carborundum, occurs as brilliant green crystals, insoluble in every common solvent. It is almost as hard as the diamond, and is used as an abrasive. It is prepared by heating a mixture of sand, coke and salt in an electric furnace.

Other elements of the Carbon group are: Germanium and Tin. Both are more metal-like in their properties than is Carbon. Their valence is 2 and 4. More remote members of the Carbon group are: Titanium, Zirconium, and Thorium. Their valence is 4. They are of rare occurrence.

BORON.

SYMBOL, B; AT. MASS, 10.9; VALENCE, III.

There are two kinds of Boron, the *crystalline* and the *amorphous*. The former resembles the diamond very closely in its

lustre, refraction of light and hardness. The amorphous is a greenish-brown powder.

Occurrence:

It is found in volcanic countries, especially in Italy, and escapes as boric acid mixed with water-steam from cracks in the ground. When these fumes are passed through a solution of Sodium-carbonate, they form Sodium-borate or borax, which may then be evaporated. Crude borax and other minerals containing boric acid are mined in California and Nevada.

OXIDE OF BORON.

Boric-oxide (B_2O_3) is a glass-like substance formed by heating boric acid, which loses its water. It is very stable. When melted, it dissolves oxides of metals and yields with many characteristic colors. It is therefore used in the detection of metals.

ACIDS OF BORON.

With water, the oxide of Boron should form three acids.

$$B_2O_3 + H_2O = 2HBO_2, \text{ meta-boric acid.}$$
$$B_2O_3 + 2H_2O = H_4B_2O_5, \text{ para-boric acid.}$$
$$B_2O_3 + 3H_2O = 2H_3BO_3, \text{ ortho-boric acid.}$$

Only the first and third of these are known; but another boric acid is obtained by the addition of one molecule of water to two molecules of Boron-trioxide:

$$2B_2O_3 + H_2O = H_2B_4O_7,$$
tetra-boric, di-boric or pyro-boric acid.

Metaboric acid (HBO_2).

META-BORIC ACID is of little importance.

Ortho-boric acid (H_3BO_3).

ORTHOBORIC ACID (*acidum boricum*) is the official form of boric acid and consists of small white crystals which are fatty to the touch. It has no color and little taste. It is soluble in cold

water 1:18, and much more soluble in hot water. It is soluble in alcohol and glycerine, and these solutions burn with a green flame.

The solutions of boric acid turn turmeric paper brown, even in the presence of hydrochloric acid.

When heated Orthoboric acid looses water and becomes meta-boric acid; and by further addition of heat. it changes to Boron-trioxide.

Boric acid is an antiseptic and disinfectant without being a poison. It is used in diseases of the eye and ear, etc. It is also met with in foods as a preservative.

Preparation:

Boric acid is prepared by making hot solutions of borax, and adding a stronger acid (nitric) to this. On cooling, the boric acid crystallises out.

The ortho-boric acid does not form salts. If treated with a base, it gives up water and forms tetra-boric acid, and this then forms a salt:

$$4H_3BO_3 = H_2B_4O_7 + 5H_2O$$

Tetra-boric acid ($H_2B_4O_7$).

This is not of importance in the free state and is only stable in dry condition. When dissolved, it at once takes up water (5 molecules) and is converted into ortho-boric acid:

$$H_2B_4O_7 + 5H_2O = 4H_3BO_3$$

Tetra-boric acid forms salts, all common borates being tetra-borates. They are white unless colored by the metal. All are insoluble in water, except those of the alkali-metals.

Tests for borates: 1, add sulphuric acid and alcohol to the substance to be tested, and ignite. If borates are present, the flame is green. 2, add water and a few drops of hydrochloric acid to the substance to be tested; a piece of turmeric paper dipped in this will turn reddish-brown if borates present.

Of other compounds of Boron, we may mention:

1. HYDROGEN-BORIDE or BORON-HYDRIDE (BH_3), a gas of

disagreable smell. It is poisonous, and is only known mixed with Hydrogen.

2. BORON-TRICHLORIDE (BCl_3), a mobile, colorless liquid, fuming in air. In is decomposed by water into hydrochloric and boric acids. It is prepared by passing Chlorine over a heated mixture of Boron-oxide and Carbon.

3. BORON-FLUORIDE (BF_3), a colorless gas of pungent smell, fuming strongly in air. It has a great affinity for water. If brought in contact with paper, it will decompose it by withdrawing the elements of water. When passed into water, a part is decomposed, forming boric and hydrofluoric acids. The hydrofluoric acid unites with the excess of Boron-fluoride, and forms a compound of the formula HBF_4, which is called hydro-fluoro-boric acid.

Hydro-fluoro-boric acid is only known in aqueous solutions. Its salts are called boro-fluorides. Boron-fluoride is best prepared by boiling fluorspar, Boron-trioxide and sulphuric acid together.

4. BORON-NITRIDE (BN). Boron unites directly with Nitrogen when the latter is passed over heated amorphous Boron. BN is a white powder, and when heated in a gas flame it produces an intense greenish-white light.

5. BORON-CARBIDE consists of black, brilliant crystals, which are even harder than carborundum. It is prepared by heating Boron-oxide together with coal in an electric furnace.

THE METALS.

All metals are solids at ordinary temperatures, with the exception of Mercury, which is a liquid but solidifies at —39° C. They are of a grayish-white color, with a few exceptions like Gold, which is yellow, and Copper, which is red. All are opaque. If a metal is heated, it melts; if further heated, it boils —but the melting points and the boiling points are different. Some metals have very low melting points; for instance, Wood's metal melts in hot water. Sodium, Potassium, Tin, Zinc, Lead and Bismuth melt easily; while Silver, Gold and especially Platinum are extremely hard to melt.

The boiling points of different metals also show the greatest diversity; some (Sodium, Potassium, Zinc) have such low boiling points that they can be distilled.

The specific gravities of the metals also vary much one from the other. Some are low, like Lithium (0.59), which metal floats on water; others are high, as those of Gold and Platinum, which are amongst the heaviest substances known.

The metals were formerly classed according to their specific gravities into (1) Light metals, those with a specific gravity of less than 5; and (2) Heavy metals, with a specific gravity of more than 5.

All metals are insoluble in ordinary solvents but dissolve only in other molten metals. In this respect they show a marked difference from the non-metals, for Iodine, Sulphur, Phosphorus, etc., have many ordinary solvents. All metals are chemically soluble in acids, the acid as well as the metal being changed, and a salt formed.

All metals are good conductors of heat and electricity, while the non-metals are not. All metals have great affinity for the halogen elements, some even igniting when brought in contact

with a halogen. Metals have also a strong affinity for Sulphur, and some of them will glow when heated with that element and form a sulphide.

The affinity of metals for Oxygen is very different in different cases, some uniting with it so energetically that they lose their brightness at once when brought into air, because a coating of the oxide is formed over them. Sodium and Potassium do this. Such metals are best kept in bottles containing kerosene. These same metals, when brought together with water, take up the Oxygen from the latter and liberate the Hydrogen. Other metals, like Iron, are not so rapidly oxidised, but take up Oxygen very gradually and change into the oxide (in the case of Iron, this process is called rusting). Some metals will only decompose water when heated. When water-steam is passed through a red-hot Iron pipe, Iron-oxide and free Hydrogen are formed. A third class of metals, like Gold and Platinum, have very little affinity for Oxygen, and can be kept in air for an indefinite length of time without losing their brightness. It is evident that only metals of the third class will be found in the metallic state in nature.

The characteristic difference between metals and non-metals is that the former are always bases, and unite with acids to form salts; while the non-metals are not bases, and do not unite with acids to form salts. In some few instances, metals may form acids as well as bases—this is the case with Manganese and Chromium.

If a metal has only one valence, it is invariably basic; but if it has several valences, some of its higher oxides may be acid-forming. The lower oxides are always basic. Manganese has a valence of 2, 3, 6, 7; it forms the following compounds:

Valence 2: basic (forms manganous salts)
Valence 3: basic (forms manganic salts)
Valence 6: acid (forms manganic acid)
Valence 7: acid (forms permanganic acid)

Mixtures of metals are called *alloys*. Brass (a mixture of Zinc and Copper), gun-metal, bell-metal, german silver, all coins, etc., are alloys. If one constituent of an alloy is Mercury, it is called an *amalgam*.

Classification of Metals.

I. The light metals — the specific gravity of which is less than 5. They have great affinity for Oxygen, acids, etc., and are therefore not found in nature in the free state but as compounds. These compounds are especially seen in salts and earths, and are colorless unless the other portion of the compound colors them. They are divided into three classes:

(i). *Alkali-metals*—Lithium, Sodium, Potassium, Rubidium, Cæsium and Ammonium. They have a valenec of 1. All except Cæsium and Rubidium are lighter than, and float on, water. They are the most energetic of the metals, especially when uniting with Oxygen, Chlorine and the acids. They are kept under kerosene, as they quickly oxidise in air. Water is decomposed by them at ordinary temperatures, Hydrogen and the oxide of the metal being formed. The latter unites with the excess of water and forms the hydroxide. Their compounds are colorless unless colored by the other components. With a few exceptions, they are all soluble in water.

(ii). *Alkali-earth metals*—Magnesium, Calcium, Strontium and Barium, with a valence of 2. These also are energetic, like the preceding class, and must be kept under kerosene. They are heavier than water, which they decompose at ordinary temperatures with the evolution of Hydrogen (Magnesium will only do this with boiling water). Their compounds are colorless unless colored by the other components. They are not as soluble as the members of the first class.

(iii). *Earth-metals*—Aluminum (specific gravity less than 5); also the rarer metals Gallium, Indium, Cerium, Thorium, Erbium, Yttrium, Scandium; Neodymium, Praseodymium, and Lanthanium. The valence of these is principally 3 . The specific gravity of these rarer metals is more than 5, and they should therefore be classed with the heavy metals; their close relationship to Aluminum, however, renders this a more fitting place for them.

II. The heavy metals — those with a specific gravity higher than 5. The majority of these form colored compounds. Gold compounds are yellow, Platinum compounds are brown, Copper compounds blue or green, Iron compounds green (Fer-

rous) or brown (Ferric), Nickel compounds green, Cobalt compounds pink or blue, Chromium compounds green, yellow and red, etc.

Some form colorless compounds, like Zinc compounds and most of the compounds of Cadmium, Lead, Silver, and Mercury.

A few of the heavy metals, like Gold and Platinum, are found in nature in the metallic state, on account of their slight affinity for Oxygen. The majority of metals, however, are found as *ores*.

These are principally the oxides and sulphides.

The most scientific method of classifying metals is according to the periodic law. We will follow this classification here.

Preparation of Metals.

1. *By reduction of the oxides*:

(a). By heating the oxide and passing Hydrogen over it. Water and the metal result:

$$CuO + 2H = Cu + H_2O$$

(b). By heating the oxide with Carbon, forming Carbon-dioxide (or monoxide) and the metal:

$$2CuO + C = CO_2 + 2Cu$$

This method is largely used technically.

(c). By heating a mixture of an oxide of the metal with another metal stronger in its affinity for Oxygen (Aluminum and Magnesium are much used). For instance, metallic Manganese can be obtained by igniting its oxides with Aluminum powder.

$$3MnO_2 + 4Al = 2Al_2O_3 + 3Mn$$

2. *From the sulphides*:

(a). By heating the sulphide with Iron filings. The Iron takes up the Sulphur, and the metal is freed:

$$HgS + Fe = FeS + Hg$$

(Aluminum powder may also be used advantageously here).

(b). By roasting the sulphide in air. The metal is converted into an oxide, and the Sulphur into Sulphur-dioxide—which, being a gas, passes off.
The oxide may then be reduced by heating in a current of Hydrogen or with Carbon. This is a much-used process.

3. *From the salts*:

(a). In the dry state.

1. The salt, usually chloride, is fused and an electric current passed through the fused mass. The metal is deposited at the negative pole:

$$AlCl_3 = Al + 3Cl$$

This is an important method for the manufacture of light metals.

2. The salt, usually the chloride, is mixed with some other metal which has greater affinity for the acid of the salt, with which it unites and liberates the metal (Sodium, Magnesium, Aluminum are much used for this purpose).

$$MgCl_2 + 2Na = 2NaCl + Mg$$

(b). From the salts in the dissolved state (only applicable to the heavy metals):

1. By passing an electric curent through the solution of a salt of the metal. The metal is deposited at the negative pole.

2. By placing in the solution of a salt some other metal which has greater affinity for the acid than the one in the original salt. The stronger metal unites with the acid and frees the weaker one. Iron, Zinc and Aluminum have strong affinities, and are much used. Copper can be prepared by placing plates of Iron in a solution of Copper-sulphate, Iron-sulphate and free Copper resulting:

$$CuSO_4 + Fe = FeSO_4 + Cu$$

If an Iron nail or a strip of Zinc is suspended in a solution Lead, Tin, Bismuth, or some other metals, the metal of the solution separates out in crystals upon the nail or Zinc-strip. The growths resulting from the accumulations of these crystals were called *arbors* or *trees* by the alchemists.

3. By converting the salt of the heavy metals into the

insoluble hydroxide by the addition of Potassium-hydroxide. Then washing and drying the precipitate obtained and changing this into the oxide by the addition of heat. The oxide is finally reduced by Hydrogen or Carbon,

Preparation of Oxides.

1. By burning the metal.

2. By heating the hydroxide, which gives up water and forms the oxide.

3. By heating the carbonate, which gives up Carbon-dioxide and forms the oxide.

4. By heating the nitrate, which gives up Nitrogen-dioxide and forms the oxide.

Preparation of the Sulphides.

1. By heating the metal with Sulphur.

2. By heating the sulphate with coal:

$$CaSO_4 + 2C = CaS + 2CO_2$$

3. If the sulphide is insoluble in water, it may be obtained as a precipitate by passing Hydrogen-sulphide through a solution of one of its salts or mixing the solution of one of its salts with Ammonium-sulphide.

Preparation of Hydroxides.

(a). *When soluble.* 1. By dissolving the metal in water. Hydrogen escapes and the hydroxide is formed. 2, Treat the oxide with water:

$$BaO + H_2O = Ba(OH)_2$$

(b). *When insoluble.* By treating a solution of the metal with a solution of a soluble hydroxide (Sodium, Potassium, Ammonium). The hydroxide of the metal previously contained in the salt precipitates.

Preparation of Chlorides, Bromides and Iodides.

1. By the direct action of the halogen upon the metal:

$$Fe + 2I = FeI_2$$

2. By dissolving the metal, or its oxide, hydroxide or carbonate in the hydrogen acid of the halogen

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

3. By reducing chlorates, bromates, or iodates by heat

$$KClO_3 = KCl + 3O \quad ,$$

or by treating them with reducing agents, which rob them of their Oxygen—as treating them with Hydrogen-sulphide or heating them with coal (this latter may cause serious explosions)

$$2KIO_3 + 3C = 2KI + 3CO_2$$

4. Insoluble chlorides, iodides and bromides can be prepared by precipitating a solution of any soluble salt of the metal with a soluble halogen salt.

Preparation of the Salts of the Metals.

The solubility is the first consideration, as it governs the method employed.

Solubility—the following table gives the solubilities of the principal salts in water:

Oxides: all insoluble but those of the alkali and alkali-earth metals (Magnesium-oxide is also insoluble).

Hydroxides: The same.

Sulphides: The same.

Chlorides: All soluble but Silver, Lead and Merous chlorides. (Lead-chloride is slightly soluble)

Bromides. The same.

Iodides: The same. Mercuric-iodide is also insoluble.

Sulphates: All soluble but those of Lead, Strontium, Barium and Calcium (the latter is sparingly soluble).

Chlorates: All soluble.

Nitrates: All soluble.

Phosphates: All insoluble except those of Sodium, Potassium and Ammonium.

Arsenates: The same.

Borates: The same.

Carbonates: The same.

Silicates: All insoluble except those of Sodium, Potassium and Ammonium when the metal is in excess.

Having determined the solubility of the salt, the procedure is as follows:

I. *If the salt is soluble.* Treat the metal or its oxide, hydroxide or carbonate with the acid then evaporate to crystallisation:

Zinc + sulphuric acid = Zinc-sulphate

II. *If the salt is insoluble.* Make two solutions, one containing a soluble salt of the acid (the Sodium salt is preferable) and the other a soluble salt of the metal (preferably sulphate, chloride or nitrate). Then mix the two solutions, and by DOUBLE DECOMPOSITION the salt required is precipitated. This is filtered off, washed and dried.

Suppose Zinc-carbonate, which is insoluble, is desired; then a solution of Sodium-carbonate and one of Zinc-sulphate are brought together:

Sodium-carbonate		Sodium-sulphate
×	form	
Zinc-sulphate		Zinc-carbonate

EXAMPLES:

How is Silver-nitrate prepared?

As all nitrates are soluble, it can be prepared by dissolving metallic Silver in nitric acid.

How is Mercuric-iodide obtained?

According to the preceding table, this is insoluble. Therefore two solutions are prepared: (a) a soluble Mercuric salt—say Mercuric-chloride in water; (b) a solution of a soluble iodide, for instance Potassium-iodide in water. On mixing the two, Mercuric-iodide is precipitated.

Preparation of Acid Salts.

Acid salts are prepared by treating the normal salt with more of the acid. Thus Sodium-bisulphate is prepared by treating Sodium-sulphate with sulphuric acid:

$$Na_2SO_4 + H_2SO_4 = 2NaHSO_4$$

Acid salts which contain a volatile acid are decomposed by heat, the excess of acid escaping and leaving the normal salt:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

Preparation of Basic Salts.

There are two general methods:

1. By treating the normal salt with water and the hydroxide or oxide of the metal of the salt. For instance, Lead-subacetate is made by boiling a solution of Lead-acetate with Lead-oxide.

2. The majority of basic salts are insoluble in water, and can be prepared by adding an excess of water to a normal salt. This decomposes the salt into free acid, which remains in solution, and a basic salt, which is precipitated. Bismuth-subnitrate is prepared by adding an excess of water to a solution of normal Bismuth-nitrate.

Group I.

This group of metals have the oxide formula E_2O, showing a valence of 1. They are divided into two subclasses:

1. The metals which belong to the main series of the first group in the periodic arrangement. They are also called the alkali-metals. Lithium, Potassium, Sodium, Rubidium and Cæsium may be placed here, and to these may be added Ammonium. We may call them family A.

2. The metals which belong to the subseries of the first group, and which are distantly related to the preceding. To this class belong Copper Silver and Gold. We may term it family B.

Family A—the Alkali Metals.

To this class belong Lithium, Sodium, Potassium, Rubidium, Cæsium and Ammonium.

SODIUM (Natrium).

SYMBOL, Na; AT. MASS, 22.88; VALENCE, I.

Sodium is a silver-white metal, soft and kneadable. It is preserved under kerosene for it is very easily oxidised. If placed on water, it floats and melts, globules of the metal rolling on the surface. The water is decomposed, Sodium-hydroxide and free Hydrogen being formed

$$Na + H_2O = NaOH + H$$

It is prepared by distilling Sodium-carbonate with coal.

Source:

Sodium is found as common salt (NaCl) in solution in sea-water, and as rock-salt in mines. It also occurs in many minerals.

Sodium-oxide, Na_2O

It is questionable if this compound exists; if Sodium is burned briskly in Oxygen, it forms Sodium-peroxide, Na—O—O—Na.

Sodium-dioxide, Na_2O_2

It is a yellowish-white solid, which forms Sodium-hydroxide and free Oxygen when in contact with water. Heat is produced by this reaction. If Sodium-dioxide is slowly added to cooled water or cold hydrochloric acid, Hydrogen-dioxide is formed:

$$Na_2O_2 + 2H_2O = H_2O_2 + 2NaOH$$

It combines with 8 molecules of water to form a crystalline compound, $Na_2O_2,8H_2O$. It has recently come into prominence as a bleaching agent, disinfectant, antiseptic, etc.

Sodium-chloride (Sodii-chloridum) $NaCl$.

occurs as white, cubic crystals, equally soluble in hot and cold water (about 1:3). It is one of the necessary food-stuffs of animals. It is prepared by the evaporation of seawater (sea salt), and is mined (rock salt). The pure white table salt is prepared by evaporating a solution of the mined salt.

Sodium-sulphate (Sodii-sulphas), Na_2SO_4

This salt is also called Glauber's salt. When crystallised, it combines with 10 molecules of water; therefore the formula is Na_2SO_4,10aq. It is official in the crystalline form, the crystals being colorless and soluble in water (1:2.8 at 15° C.); the crystals are efflorescent and fall to a white powder when exposed to air. It is prepared by treating common salt with sulphuric acid. Sodium-sulphate and hydrochloric acid are formed:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

Sodium-carbonate (Sodii carbonas), Na_2CO_3

This is a colorless, crystalline body, soluble in water (1:16 at 15° C.). When crystallised out it has 10 molecules of water and the formula is thus Na_2CO_3,10aq. It is also called *sal soda* or *washing soda*. It is efflorescent, and its solution has a strong alkaline reaction and taste. After undergoing efflorescence, the white crystalline residue still contains 1 molecule of water of crystallisation, corresponding to about 14.5 percent. It is official

as Sodii carbonas monohydratus. When subjected to a temperature of over 50°, it loses all water of crystallisation.

Crude exsiccated Sodium-carbonate is technically called *soda ash* or *black ash* and is of great importance, being used for the preparation of soap, glass and other Sodium compounds. Its manufacture, together with that of sulphuric acid, is a very important chemical reaction. It is prepared as follows:

I *The LeBlanc or black ash process.* 1. Common salt is treated with sulphuric acid, and Sodium-sulphate and hydrochloric acid are formed:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

2, The Sodium-sulphate is heated with coal and chalk (Calcium-carbonate). The coal takes up the Oxygen, and forms Sodium-sulphide and Carbon-dioxide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

The Sodium-sulphide with the Calcium--carbonate forms, by double decomposition, Calcium-sulphide and Sodium-carbonate.

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

Sodium-carbonate is soluble in water, while Calcium-sulphide is not; therefore, if the mass is treated with water, the Sodium-carbonate can be dissolved out, filtered, and the filtrate evaporated to crystallisation.

II. *The Ammonia Soda process.* Carbon-dioxide gas is obtained by heating Calcium-carbonate. The CO_2 gas is passed into strong ammonia-water, where it forms Ammonium-bicarbonate in solution. This is then treated with Sodium-chloride, and Ammonium-chloride and Sodium-bicarbonate are formed:

$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl$$

The solution is very concentrated, and the Sodium-bicarbonate, being least soluble, precipitates and can be filtered off and dried. This Sodium-bicarbonate is heated, and it then forms Sodium-carbonate, while Carbon-dioxide and water escape. The filtrate containing the Ammonium-chloride can be again converted into ammonia-water by distilling with slaked lime.

Sodium-bicarbonate (*Sodii-bicarbonas*), $NaHCO_3$

This is also called acid Sodium-carbonate or mono-Sodium-carbonate, and is a white powder of faint alkaline taste and reaction. It is familiarly known as *saleratus* or *baking soda*. Its solubility in water is 1:12, and it may be prepared by treating moist Sodium-carbonate with Carbon-dioxide:

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

When Sodium-bicarbonate is heated, it decomposes and forms Sodium-carbonate, water, and Carbon-dioxide:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

This decomposition takes place at temperatures below 100° C. In dissolving Sodium-bicarbonate, then, cold water should be used, as hot water will cause the Carbon-dioxide to escape and the solution to effervesce.

Sodium-sulphite (*Sodii sulphis*), Na_2SO_3

A colorless salt, soluble in water. It contains 7 molecules of water of crystallisation, and its formula is Na_2SO_3,7aq. It is efflorescent. It may be prepared by mixing a solution of Sodium-bisulphite with one of Sodium-carbonate until the reaction is weakly alkaline, and then evaporating.

Sodium-bisulphite (*Sodii-bisulphis*), $NaHSO_3$

White crystals, exhaling an odor of Sulphur-dioxide; soluble in water. It is prepared by passing Sulphur-dioxide through a concentrated solution of Sodium-carbonate; Sodium-bisulphite separating as opaque crystals.

Sodium-thiosulphate (*Sodii-thiosulphas*), $Na_2S_2O_3$

Colorless salt, easily soluble in water; it contains 5 molecules of water of crystallisation, $Na_2S_2O_3$,5aq. It is prepared by boiling a solution of Sodium-sulphite with Sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3$$

It is also called Sodium-hyposulphite or 'hypo,' and is used in photography.

Sodium-nitrate (*Sodii-nitras*), $NaNO_3$

Occurs as colorless crystals, soluble in water and somewhat deliquescent. On account of the latter property, it cannot be employed in the manufacture of gunpowder. It is mined in Chili, and comes on the market under the name 'Chili saltpeter.'

Sodium-nitrite (*Sodii-nitris*), $NaNO_2$

A white, deliquescent mass, very soluble in water. It is prepared by heating Sodium-nitrate with Lead or Copper:

$$NaNO_3 + Pb = NaNO_2 + PbO$$

Sodium-phosphate (*Sodii-phosphas*), Na_2HPO_4

Colorless, efflorescent crystals, containing 12 molecules of water of crystallisation. It is soluble in water, and may be prepared by treating Sodium-carbonate with phosphoric acid. Its reaction is slightly alkaline with litmus and phenol-phthalein. It is official in crystal form, and also as an exsiccated salt (*Sodii phosphas exsiccatus*).

Sodium-pyrophosphate (*Sodii-pyrophosphas*), $Na_4P_2O_7$

Colorless crystals, soluble in water and permanent in air. Prepared by heating Sodium-phosphate, which loses water:

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7$$

Sodium-hypophosphite (*Sodii-hypophosphis*), NaH_2PO_2

White, deliquescent salt, soluble in water. It is a strong reducing agent. When heated, it gives up self-inflammable phosphine.

Prepared by boiling Phosphorus with water and Sodium-hydroxide. It should never be triturated with oxidising agents, (chlorates, nitrates, etc.), as an explosion is liable to result.

Sodium-arsenate (*Sodii-arsenas*), Na_2HAsO_4

Colorless, efflorescent crystals, soluble in water. It is isomorphous with Sodium-phosphate, and both contain 12 molecules of water of crystallisation. It is prepared by treating Sodium-carbonate with arsenic acid. It enters the official *liquor Sodii arsenatis*, a colorless liquid containing 1 percent of Sodium-

arsenate, previously deprived of its water of crystallisation and then dissolved in water. It is also official in exsiccated condition (*Sodii arsenas exsiccatus*).

Sodium-borate (*Sodii-boras*), $Na_2B_4O_7$

Also called *borax,* and bi- or tetra-borate of Sodium. It forms colorless crystals, soluble in water, and containing 10 molecules of water of crystallisation. It is efflorescent. It may be prepared by treating Sodium-carbonate with boric acid. If heated, exsiccated borax melts and forms a colorless liquid which dissolves the oxides of metals with characteristic colors. This is made use of in blow-pipe analysis.

Sodium-chlorate (*Sodii-chloras*), $NaClO_3$

This resembles very closely Potassium-chlorate. It occurs as colorless crystals, soluble in water. When triturated with burnable substances, it causes an explosion. Heated, it evolves Oxygen and forms the chloride. When treated with hydrochloric acid, it forms Sodium-chloride and free Chlorine. It is prepared by passing Chlorine gas through a hot solution of Sodium-hydroxide, Sodium-chloride and Sodium-chlorate being formed. These can be separated by crystallisation. The separation of the two is difficult, as both are very soluble; and it is advisable to mix solutions of Sodium-bitartrate and Potassium-chlorate; Sodium-chlorate goes into solution and Potassium-bitartrate precipitates.

Sodium-hydroxide (*Sodii hydroxidum*), $NaOH$

This is also called *soda* or *caustic soda* or *hydrate of sodium.* It forms white, solid pieces, deliquescent and freely soluble in water, there producing heat. It will absorb Carbon-dioxide from the air and form Sodium-carbonate. For this reason and on account of its deliquescence, it should be kept in well-closed bottles. It acts as a caustic, and has strong alkaline reaction. It is official in two forms, in sticks and in a 5 percent solution under the name *liquor Sodii hydroxidi.* This liquor should be kept in bottles with a glass stopper coated with paraffin to prevent sticking, as the liquid rapidly absorbs Carbon-dioxide

from the air and forms Sodium-carbonate, which solidifies between stopper and neck. Sodium-hydroxide is prepared by boiling Sodium-carbonate with slaked lime:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$$

The Calcium-carbonate, being insoluble, precipitates and the Sodium-hydrate remains in solution. The liquid is allowed to settle, and the solution is then poured off from the sediment, evaporated to dryness, melted and the molten mass poured into Silver moulds.

Sodium-bromide (Sodii-bromidum), NaBr

White, soluble salt, without water of crystallisation. It has a pure salty taste without being bitter. It is prepared by treating a solution of Sodium-hydroxide with Bromine, forming bromate and bromide of Sodium:

$$6NaOH + 6Br = NaBrO_3 + 5NaBr + 3H_2O$$

The solution is then evaporated to dryness, and the residue mixed with charcoal powder and heated. The charcoal takes up Oxygen from the Sodium-bromate, which becomes Sodium-bromide. The whole is then dissolved in water, filtered, and the solution evaporated to crystallisation.

Sodium-iodide (Sodii-iodidum), NaI

A white salt, soluble in water, containing no water of crystallisation. It has a salty and bitter taste. It is prepared by a similar process to that used to obtain Sodium-bromide, using Iodine instead of Bromine.

Tests for Sodium: 1, It colors a non-luminous flame yellow. 2, It yields a precipitate with a solution of Potassium-pyro-antimonate.

POTASSIUM (Kalium)

SYMBOL, K; AT. MASS, 38.86; VALENCE, I.

The metal Potassium is analagous to Sodium in every respect. It is a Silver-white, soft metal, which decomposes water. It is

melted during the reaction, and the Hydrogen of the water is freed and ignited by the heat produced. The globules of the metal roll on the surface of the water and gradually decrease in size till all is dissolved. The liquid then contains a solution of Potassium-hydroxide.

It is prepared by distilling Potassium-carbonate with coal.

There are two sources of Potassium: (1), it is contained as Potassium-carbonate in wood ashes. (2), it occurs in the mineral *sylvite*, which is Potassium-chloride (KCl). This is mined in large quantities at Strathfurth in Germany.

Potassium-peroxide (*Potassii-dioxidum*), K_2O_2

Very similar to Sodium-peroxide (which see).

Potassium-chloride (*Potassii-chloridum*), KCl

White crystals, soluble in water. Occurs as *sylvite*.

Potassium-sulphate (*Potassii-sulphas*), K_2SO_4

Hard, transparent prisms, or white odorless powder; soluble in water. Prepared by treating Potassium-carbonate or Potassium-choride with sulphuric acid.

Potassium-carbonate (*Potassii-carbonas*), K_2CO_3

A white salt of sharp, alkaline taste, deliquescent and readily soluble in water; containing no water of crystallisation. It cannot be crystallised on account of its great solubility. The crude form is prepared as follows: 1, from the Potassium-chloride according to the LeBlanc process, by converting it into Potassium-sulphate by sulphuric acid, and then heating the sulphate with coal and chalk. 2, from wood ashes, by dissolving the ashes in water and evaporating the solution to dryness. This comes on the market under the name of *Canadian* or *American Pearl-ash*.

Chemically pure Potassium-carbonate is prepared as follows: 1, by heating pure cream of tartar, which decomposes into Carbon and Potassium-carbonate. The latter is dissolved out,

filtered, and evaporated to dryness. This method of preparation gave rise to the name 'salt of tartar,' which is a synonym for Potassium-carbonate. 2, by heating pure Potasium-bicarbonate, which decomposes into the carbonate, Carbon-dioxide and water:

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2$$

Potassium-bicarbonate (Potassii-bicarbonas), $KHCO_3$

White crystals, soluble in water, but less soluble than the carbonate. It can therefore be crystallised, and this offers one method for its purification. On being heated, it decomposes into Potassium-carbonate, water and Carbon-dioxide, this decomposition occurring below 100° C. This salt, then, should not be dissolved in hot water. It is prepared by dissolving Potassium-carbonate in water, and passing a current of Carbon-dioxide through the solution.

Potassium-nitrate (Potassii-nitras), KNO_3

Also called *saltpeter* and *niter*. Forms colorless crystals containing no water of crystallisation; nor is it deliquescent. It is easily soluble in water (1:3.6 at 15°). The taste is cooling and salt-like. It can be mixed with burnable substances, but these mixtures are explosive when heated. It is much used in the preparation of gunpowder, which contains saltpeter, Sulphur and Carbon. It is also used for salting meats.

There are two methods of preparing saltpeter: 1, the old method of mixing animal refuse with chalk, and allowing this to stand in piles which are frequently moistened; the decaying matter forms ammonia, which is oxidised by the air to nitric acid:

$$NH_3 + 4O = H_2O + HNO_3$$

The nitric acid combines with the chalk and forms Calcium-nitrate; the heaps are then treated with water, and a solution of Calcium-nitrate is obtained. This is treated with a solution of Potassium-carbonate, and insoluble Calcium-carbonate precipitates while Potassium-nitrate goes into solution:

$$K_2CO_3 + Ca(NO_3)_2 = 2KNO_3 + CaCO_3$$

This is filtered, and the filtrate evaporated to crystallisation.
2, A hot, concentrated solution of Chili saltpeter ($NaNO_3$) and

of Potassium-chloride are mixed together. By double decomposition Potassium-nitrate and Sodium-chloride are formed:

$$KCl + NaNO_3 = NaCl + KNO_3$$

Sodium-chloride, being least soluble in hot water, precipitates out. The filtrate from this contains the Potassium-nitrate, which may be crystallised.

Potassium-nitrite (*Potassii-nitris*), KNO_2

Similar to Sodium-nitrite, and prepared by the same method:

$$KNO_3 + Pb = PbO + KNO_2$$

Potassium-hypophosphite (*Potassii-hypophosphis*), KPO_2H_2

Similar to Sodium-hypophosphite (which see).

Potassium-chlorate (*Potassii-chloras*), $KClO_3$

White, plate-like crystals, soluble in water (1:16 at 15° C.). A strong oxidising agent. When heated, it splits into Oxygen and Potassium-chloride. If triturated with burnable bodies, as coal, sugar, Sulphur, tannic acid, etc., it explodes. Great care should therefore be exercised in mixing it, and this should be performed on paper by means of a soft spatula. It explodes if brought in contact with sulphuric acid. If treated with hydrochloric acid, it liberates Chlorine gas.

Potassium-chlorate is prepared by passing Chlorine through a hot solution of Potassium-hydrate, Potassium-chloride and Potassium-chlorate being formed. Their solubilities are different, and they are separated by crystallisation.

Potassium-hydroxide (*Potassii-hydroxidum*), KOH

This is also called *lye* and *caustic potash,* and its properties and preparation are similar to those of Sodium-hydroxide. It is also official in two forms, in sticks and in a 5 percent solution (*liquor Potassii hydroxidi*).

Potassium-bromide (*Potassii-bromidum*), KBr

Colorless or white odorless crystals of a pure salty taste. It is permanent in air, and its solubility in water is 1:1.5. Is is prepared in the same way as Sodium-bromide (which see).

Potassium-iodide (*Potassii-iodidum*), *KI*

Colorless or white crystals, of a saline and bitter taste. It is stable in dry air. Solubility in water, 1:0.7. Prepared in the same manner as the corresponding Sodium compound.

Liver of Sulphur (*Hepar sulphuris*)

Liver-colored lumps, having the disagreable smell of Hydrogen-sulphide. It must be kept in well-closed bottles, for it is deliquescent; further, it is decomposed by air, taking up Oxygen and forming carbonate and sulphate of Potassium. Chemically, liver of Sulphur is a mixture of Potassium-sulphide, polysulphides of Potassium, and Potassium-thiosulphate. It is prepared by melting Potassium-carbonate with Sulphur, and pouring the molten mass onto marble slabs.

Tests for Potassium: 1, It colors a non-luminous flame violet. 2, With Platinum-chloride, it gives a yellow precipitate. The addition of alcohol facilitates this. 3, With a concentrated solution of tartaric acid and alcohol, it gives a white, crystalline precipitate of cream of tartar.

AMMONIUM.

SYMBOL, NH_4; VALENCE, I.

Does not exist in the free state, but forms many important *Ammonium salts*. They are white unless the acid colors them, and, with few exceptions, are soluble. When heated, they volatilise. They are prepared as follows: 1, By treating ammonia or Ammonium-carbonate with the acid. 2, By subliming Ammonium-sulphate with a Sodium, Potassium, Calcium salt of a volatile acid of which the Ammonium salt is desired.

Ammonium-hydroxide, NH_4OH

Contained in aqua ammonia (see Nitrogen).

Ammonium-sulphate (*Ammonii-sulphas*), $(NH_4)_2SO_4$

A white salt, soluble in water, prepared by treating ammonia

or Ammonium-carbonate with sulphuric acid:

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$$

Ammonium-nitrate (Ammonii-nitras), NH_4NO_3

White salt, soluble in water. When heated to redness, it decomposes into water and laughing gas.
It is prepared by treating Ammonium-carbonate with nitric acid.

Ammonium-chloride (Ammonii-chloridum), NH_4Cl

A white salt of sharp taste, soluble in water. It produces material reduction of temperature on being dissolved. It is kept in pharmacies in two forms: 1, In small crystals or powder, known as Ammonium-muriate. This is prepared by treating ammonia-water or Ammonium-carbonate with hydrochloric acid. 2, In lumps, called 'sal ammoniac,' much used for soldering, etc. This form is prepared by subliming a mixture of Ammonium-sulphate and Sodium-chloride, or by subliming the material obtained by the first method.

Ammonium-bromide (Ammonii-bromidum), NH_4Br

A white salt, soluble in water, prepared by treating ammonia-water with hydrobromic acid. The best method of preparation is to add Bromine and water to Iron filings. Iron-bromide is formed. The solution is filtered and ammonia added, and a precipitate of Iron-hydroxide results while Ammonium-bromide goes into solution.

$$FeBr_2 + 2NH_4OH = 2NH_4Br + Fe(OH)_2$$

This is then filtered and the solution evaporated to dryness.

Ammonium-iodide (Ammonii-iodidum), NH_4I

A white salt of sharp, salty and bitter taste, soluble in water. It is prepared in the same way as Ammonium-bromide, using Iodine in place of Bromine. When exposed to air, it oxidises and becomes brown or yellow, and Iodine separates off. When thus oxidised, it should not be used for pharmaceutical purposes. It can be restored by making a solution of it, adding a few drops of Ammonium-sulphide, filtering and evaporating to dryness.

Ammonium-sulphide (Ammonii sulphidum).

Is much used as a test solution in analytical chemistry, in place of Hydrogen-sulphide in alkaline solutions. The test-solution, when freshly prepared, is colorless; it soon becomes yellow, however. It has a disagreeable smell, and is prepared by passing Hydrogen-sulphide into ammonia-water until it is saturated. Ammonium-sulph-hydrate (NH_4SH) forms, and this unites with the excess of ammonia-water to form Ammonium-sulphide.

Ammonium-carbonate (Ammonii-carbonas)

The official one is a mixture of Ammonium-bicarbonate (NH_4-HCO_3) and Ammonium-carbamate ($NH_2.CO.ONH_4$). It is a hard, translucent salt of ammoniacal odor. It is soluble in water, only partly (the carbamate) in alcohol. When heated, it completely volatilises. When treated with water, the carbamate part changes to normal carbonate, and the aqueous solution thus contains a mixture of Ammonium-carbonate and bicarbonate. When boiled, both split into ammonia gas and Carbon-dioxide. It is used for baking, for when heated the gases escape and create interspaces which 'lighten the bread.'

It is prepared by mixing Ammonium-sulphate and Calcium-carbonate, and subliming the mixture.

Tests for Ammonium. 1, With Platinic-chloride and alcohol it gives a yellowish, crystalline precipitate. 2, With a solution of tartaric acid in excess and alcohol, it gives a white precipitate. 3, When an Ammonium salt is treated with Potassium-hydroxide or Sodium-hydroxide, it evolves ammonia gas. This can be detected by the odor, by its action on litmus paper, or by the fact that when a glass-rod moistened with hydrochloric acid is held over the solution, white fumes are formed. 4, Nessler's solution (a solution of Mercuric-iodide in a solution of Potassium-iodide and Potassium-hydroxide) gives a yellow or brown coloration, or a reddish-brown precipitate, with Ammonium salts.

Differential test for Ammonium and Potassium: Test a small portion for Ammonium according to 3. If present, the remainder of the sample submitted for examination is placed

in a crucible, evaporated, and the dry residue heated; all Ammonium salts, being volatile, will escape. The fixed Potassium salts are left in the crucible, and may be tested for in the usual way.

LITHIUM

SYMBOL, Li; AT. MASS, 6.98; VALENCE, I.

A Silver-white metal, the lightest of all the metals, floating even on kerosene. It is of frequent occurrence, but is found only in small quantities. The waters of Lithium-springs and a few rare minerals contain it. It decomposes water, like Sodium and Potassium. Its salts have the property of dissolving uric acid calculi. All Lithium salts impart a beautiful crimson color to the flame, and this furnishes a test for them. All are readily soluble in water but the carbonate, which is only soluble with difficulty, and the phosphate, which is slightly soluble. They are white or colorless unless the acid colors them.

Lithium-carbonate (Lithii carbonas), Li_2CO_3

A white powder of alkaline taste, more soluble in cold than in hot water; about 75 parts of cold water will dissolve 1 part of the salt, while 140 parts of hot water are needed for the same purpose. It is prepared by heating the minerals containing Lithium, and then treating them with strong sulphuric acid. This dissolves out the Lithium, and also whatever Iron, Potassium, Sodium and Aluminum may be present. The filtrate is evaporated, and heated to expel the excess of sulphuric acid. It is then dissolved in water and boiled with milk of lime, which precipitates Iron and Aluminum. The filtrate is concentrated by evaporation, and precipitated with a concentrated solution of Sodium-carbonate, a precipitate of Lithium-carbonate being obtained.

RUBIDIUM and CÆSIUM

Rb=84.8 Cs=131.9

VALENCE, I.

These are rare alkali-metals, which occur in some few minerals. They were discovered by means of the spectroscope, by

Bunsen and Kirchhoff in 1860. Rubidium gives a spectrum with two red and two violet lines, and Cæsium one with two blue lines.

Group I—Family B.

COPPER, SILVER AND GOLD.

These are only distantly related to the alkali-metals, belonging to the subseries of the first group in Mendeljeff's table. They are not so energetic in their chemical action as the alkali-metals, and do not combine with water or the free Oxygen of the air. They are therefore found in the metallic state in nature. Silver shows in the formulae of its compounds the greatest similarity to the alkali-metals of any member of this group; its valence being 1. Copper, however, forms two classes of compounds—Cuprous, in which this element has a valence of 1, and Cupric, in which the valence is 2. As the latter compounds are of the most importance, Copper seems to be somewhat misplaced in the first group.

Gold also forms two kinds of compounds—Aurous compounds, in which the metal has a valence of 1; and Auric compounds, in which Gold is trivalent. The auric compounds are much more important than the Aurous, and Gold, too, appears to be hardly a typical element of the first group.

SILVER (Argentum).

SYMBOL, Ag; AT. MASS, 107.12; VALENCE, I.

It is a white metal, with a specific gravity of 10.5, melting at a temperature of about 1000° C. It dissolves easily in nitric acid, forming Silver-nitrate. It does not oxidise in air, but turns black by the action of Hydrogen-sulphide. It is found in the metallic state, in combination with Sulphur, and in may Lead ores (as in galena).

The Silver salts are, with few exceptions, white. They are easily decomposed by light, the contact of particles of organic

matter, etc.; they are thus reduced to the metallic state, and appear black. Therefore, in the preparation of medicaments containing Silver salts, no organic matter should be used.

Silver-nitrate (Argenti nitras), $AgNO_3$

It is official in three forms: 1, As crystals (*Argenti nitras*), a colorless salt, easily soluble in water, prepared by dissolving metallic Silver in nitric acid, and then evaporating the solution to crystallisation. 2, Moulded Silver-nitrate (*Argenti nitras fusus*), also called 'lunar caustic,' prepared by melting Silver-nitrate crystals, after adding a few drops of hydrochloric acid, and pouring the mass into pencil-shaped Silver moulds. The hydrochloric acid which is added forms a small amount of Silver-chloride, rendering the pencils of Silver-nitrate less brittle. 3, Diluted Silver-nitrate (*Argenti nitras mitigatus*), also called 'mild lunar caustic,' is prepared by melting together one part of Silver-nitrate and 2 parts of saltpeter, and pouring the fused mass into Silver moulds.

Silver-oxide (Argenti oxidum), Ag_2O

A blackish-brown powder, insoluble in water. It gives up Oxygen readily, and explodes when triturated with burnable bodies. It forms an explosive compound with aqua ammonia. It is prepared by adding Potassium-hydroxide to a solution of Silver-nitrate:

$$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O$$

Silver-chloride (Argenti chloridum), AgCl

A white powder, insoluble in water and acids, but soluble in aqua ammonia, Potassium-cyanide, Sodium-thiosulphate. It blackens on exposure to light, and is therefore used in photography. It is prepared by precipitating a solution of Silver-nitrate with hydrochloric acid or other soluble chloride:

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

Iodide and Bromide of Silver, AgI, AgBr

The color of the bromide is almost white; the iodide is yellow. They possess the same general properties as the chloride,

but the iodide is insoluble in diluted ammonia-water; the bromide is soluble, but not nearly so readily as the chloride. They are prepared by precipitating Silver-nitrate with Potassium-bromide or Potassium-iodide:

$$AgNO_3 + KBr = AgBr + KNO_3$$

Their most important use is in photography.

PHOTOGRAPHY.

Photography was practised by a frenchman named Daguerre in the early part of the nineteenth century. It is based on the fact that Silver salts, especially the bromide and iodide, are reduced to the metallic state by light. The photographic plate is a piece of glass coated on one side with a solution of gelatin to which has been added Silver-nitrate and a soluble bromide. The plate will now possess a coating of Silver-bromide.

This plate is exposed to the light of the subject to be photographed, and the Silver-bromide is decomposed. The exposure is not continued until the blackened Silver is visible; but only long enough to make the Silver-bromide at the points where the light acts more easily reduceable than the remainder of the Silver-bromide on the plate. In other words, the points exposed have become *sensitised.* The plate is then treated with a *developer,* as pyrogallic acid, which reduces the sensitised Silver-bromide, and renders the picture visible. The excess of the Silver salt is now removed by washing in 'hypo' (Sodium-thiosulphate) which dissolves the Silver bromide but not the metallic Silver, and the plate, called now the *negative,* may be exposed to light without undergoing any change. The dark spots in the original look light in the negative, and vice versa. The positive or true picture may be obtained from this by backing it with a photographic paper, and exposing to light. The true picture formed upon the paper is fixed in the same way as the plate.

Tests for Silver: 1, With hydrochloric acid or other soluble chloride it gives a white precipitate of Silverchloride, soluble in ammonia-water; the precipitate is reformed on the addition of nitric acid. 2, With Hydrogen-sulphide it gives a black precipitate in any solution.

COPPER (Cuprum).

SYMBOL, Cu; AT. MASS, 63.1; VALENCE, (I) II.

Copper is a red metal, soluble in boiling sulphuric acid and easily in nitric acid. When dissolved in the former, Sulphur-dioxide escapes; in the latter, Nitrogen-dioxide or Nitrogen-monoxide are freed. Other acids dissolve Copper only when the metal is alternately dipped into acid and brought into air; hence Copper is soluble where it meets air and acid. Fruit may be boiled in Copper vessels without danger of the fruit acids attacking the vessel, as the escaping steam drives all air out.

Copper is easily affected by ammonia-water in the presence of air, its solution becoming dark blue. Carbon-dioxide acts upon metallic Copper if moisture is present, and forms green Copper-subcarbonate.

Many important alloys contain Copper, among them being brass, german silver, bell metal, gunmetal, bronze, etc.

Copper is found in nature in the metallic state, and as carbonate (malachite), and sulphide (Copper-glance, Copper-pyrite).

The methods for the preparation of Copper vary greatly, because of the different composition of the Copper ores.

CUPROUS COMPOUNDS.

In these, Copper is univalent. The salts are colorless, and are powerful reducing agents. They readily take up Oxygen from the air or from its compounds and are converted into blue Cupric salts. A few insoluble Cuprous compounds are not colorless. They are:

Cuprous-oxide, Cu_2O

A bright-red powder, insoluble in water but soluble in acids, forming the Cuprous salts. It occurs in nature as *cuprite*. It is prepared by boiling a solution of grape-sugar with Copper-sulphate and Potassium-hydrate (see sugar test). When fused with glass, it colors the latter ruby-red.

Cuprous-hydroxide, $CuOH$

A yellow, amorphous powder, insoluble in water. Also formed in sugar tests.

Cuprous-sulphide, Cu_2S

A black substance found in nature.

CUPRIC SALTS.

These are the more common of the Copper compounds, and unless otherwise specified Copper salts are assumed to be in the Cupric condition. Here the metal is bivalent. In hydrated condition, the salts are blue or green, the Cupric ion being blue. In anhydrous condition, many are yellow; and the green color of some of the hydrated Cupric salts is due to the fact that only part of the compound is ionised and blue, and this, with the yellow portion which is not ionised, produces a green coloration.

Cupric nitrate (Cupri nitras), $Cu(NO_3)_2$

Blue crystals, easily soluble in water. Prepared by dissolving metallic Copper in nitric acid.

Copper-sulphate (Cupri sulphas), $CuSO_4$

This is commonly known as *blue vitrol.* It occurs as blue crystals, containing 5 molecules of water of crystallisation. It is soluble in water (1:2.2). It may be prepared by dissolving metallic Copper in boiling sulphuric acid. When the water of crystallisation is driven out by heat, the residue—anhydrous Copper-sulphate—is white.

Cupric-oxide (Cupri oxidum), CuO

This is a black powder, insoluble in water but soluble in acids It is prepared by heating Copper-nitrate. It can be heated without suffering any change; but if heated with reducing agents it oxidises them.

This property of oxidation is of importance in the analysis of organic substances.

Elementary Analysis of Organic Substances.

A known quantity of the organic substance to be analysed which always contains Carbon and Hydrogen is mixed with Cupric-oxide and placed in a thick-walled glass tube which is sealed at one end and heated. The elements Carbon and Hydrogen forms oxides with Oxygen from the Copper-oxide, and these pass over as gases. The gases are led through a Calcium-chlor-

ide tube of known weight, where the Hydrogen-oxide (water) is taken up by the Calcium-chloride; then through a bottle of Potassium-hydrate, of known weight, where the Carbon-oxide is absorbed. The amount of Hydrogen and of Carbon in the organic body can be computed from the increase in weight of the apparatus.

Cupric-hydroxide (*Cupri hydroxidum*), $Cu(OH)_2$

A blue powder, insoluble in water but soluble in acids, ammonia-water sugar and Rochelle salt. The solutions in the two latter solvents have a beautiful dark-blue color. The blue solution in ammonia dissolves cellulose, cotton, paper, etc. Copper-hydroxide is prepared by precipitating a solution of Copper-sulphate with one of Potassium-hydroxide. When the blue hydrate of Copper is heated, it loses water and forms the black Copper-oxide. This decomposition takes place below 100° C., and therefore occurs when Copper-hydroxide is boiled. If the blue Copper-hydroxide is boiled with sugar in an alkaline solution, it gives off a part of its Oxygen to the sugar, and is converted into yellow Cuprous-hydroxide and later into red Cuprous-hydroxide and later into red Cuprous-oxide, which sinks to the bottom of the solution. This is applied in the sugar tests.

Sugar tests with Copper.

1. *Trommer's test.* Add to the solution to be tested a few drops of a Copper-sulphate solution and some Potassium-hydroxide solution, and boil. If sugar is present, the blue color of the Copper-sulphate is changed to yellowish-red; if no sugar is present, the Copper-sulphate gets black.

2. *Fehling's test.* Fehling's solution is used, and this is a dark-blue liquid, consisting of Copper-sulphate, Potassium-hydroxide and Rochelle salt which dissolves the Copper-hydroxide formed. If this solution is boiled, it undergoes no change; but if boiled with sugar, a red precipitate of Cuprous-oxide is formed.

Cupric-chloride (*Cupri chloridum*), $CuCl_2$

A green salt, readily soluble in water. The concentrated solution is green, the diluted blue. It is prepared by dissolving

oxide, carbonate or hydroxide of Copper in hydrochloric acid. It is formed when concentrated solutions of Sodium-chloride and Copper-sulphate are mixed; the blue color is seen to become green.

Tests for Copper. 1, The addition of an excess of ammonia-water develops a blue color. 2, With Potassium-ferro-cyanide a red precipitate of Copper-ferro-cyanide is produced. 3, With Hydrogen-sulphide a black precipitate is produced in any reaction. 4, When a bright piece of Iron is placed in a Copper solution, the Iron acquires a red coating of Copper.

GOLD (Aurum).

SYMBOL, Au; AT. MASS, 195.7; VALENCE, I, III.

Gold is a yellow metal, very hard to melt, and amongst the heaviest of known substances—its specific gravity is between 19 and 20. It is insoluble in all solvents except Chlorine and liquids containing free Chlorine (nitro-hydrochloric acid), and when these act upon it, Auric-choride is formed. It does not oxidise in air. It can be beaten into extremely thin leaves, which appear green by transmitted light. Alloys of Gold are usually employed, as the metal itself is very soft and wears quickly. In nature it occurs in quartz in small pieces; rivers passing over such quartz frequently carry the Gold along and deposit it in the sand. It is obtained from this sand or by crushing the quartz: 1, By washing it in running water, which removes the sand but leaves the heavier Gold. 2, By treating the sand or powdered rock with Mercury, which dissolves the Gold; the solution obtained is heated, and the Mercury distils over, but not the Gold. 3, By grinding and roasting the rocks, and treating the powder with Chlorine and water, which dissolves the Gold: the solution obtained is filtered and treated with Ferrous-sulphate, which separates the Gold. 4, By the cyanide process. The powdered rocks are treated with a weak solution of Potassium-cyanide in the presence of air; this dissolves the Gold; the solution is then filtered and an electric current passed through it, and the negative pole collects the Gold.

The Aurous compounds, in which Gold is univalent, are un-

stable. The Auric compounds, in which the metal is tri-valent, are more stable than the preceding, but are also easily decomposible. They are usually yellow. The most important is

Auric-chloride (*Auri chloridum*), $AuCl_3$

A yellow salt, easily soluble in water. Prepared by dissolving metallic Gold in nitro-hydrochloric acid and evaporating the solution to dryness. It is decomposed by light. It is official mixed with 50 percent common salt (*Auri et Sodii chloridum*). This preparation contains about 30 percent of metallic Gold, which can be determined by heating to redness, which causes Chlorine to escape and metallic Gold to be left. When water is added, the common salt dissolves but not the Gold; this can be separated by filtration.

Auric-chloride combines with hydrochloric acid to form the compound

$$AuCl_3 + HCl = HAuCl_4$$

which is known as *hydro-chlor-auric acid.* It forms salts, the official Gold- and Sodium-chloride being a salt of this acid.

Auric-oxide (*Auri oxidum*), Au_2O_3

A brown powder which, on being heated, decomposes into Gold and Oxygen. With ammonia, it forms a very explosive compound, *Gold fulminate.* Auric-oxide has weak basic and acid properties. It dissolves in alkalies and forms salts of *auric acid* ($Au_2O_3 + H_2O = 2HAuO_2$). The salts of this acid are *aurates.*

Tests for Gold. 1, Hydrogen-sulphide gives a dark-brown precipitate, soluble in yellow Ammonium-sulphide. 2, Oxalic acid precipitates metallic Gold (brown). The liquid looks blue or green by transmitted light, and red in reflected light. 3, Ferrous-sulphate behaves in like manner. 4, Stannous-chloride throws down a purple precipitate, the *purple of Cassius.*

The Second Group of Metals.

The metals of this group have the oxide formula E_2O_2 or EO, showing them to have a valence of 2. They are subdivided into two families, A and B.

Family A—members of the main series of the second group, and are also called the *alkali-earth metals.* Glucinum (sometimes called Beryllium), Magnesium, Calcium, Strontium, Barium and Radium belong to this family.

Famliy B—metals which belong to the subseries of the second group, inserted between the principal members of the group, and only distantly related to the alkali-earth metals. They are: Zinc, Cadmium and Mercury.

Group II—Family A
The Alkali-earth metals.

Beryllium and Radium are rare. We will first study

MAGNESIUM (24.18), CALCIUM (39.8),
STRONTIUM (86.94), BARIUM (136.4).

The valence of these elements is 2. They are not found in nature in the metallic state, but in salt form—especially as carbonates and sulphates. Their salts are colorless, unless the acid colors them. Their carbonates, borates, phosphates and silicates are insoluble. The sulphates decrease in solubility in the order of their atomic masses; Magnesium-sulphate is the most soluble, Barium-sulphate the least (the latter is insoluble). The oxides and hydroxides increase in solubility with increasing atomic masses; Magnesium-hydroxide is the least soluble, Barium-hydroxide the most.

MAGNESIUM.

SYMBOL, Mg; AT. MASS, 24.18; VALENCE, II.

This is a silver-white, light metal, which becomes dull in air by oxidation. It slowly decomposes boiling water, freeing Hydrogen. It will ignite if heated in air, and burns with a bright light, forming a white smoke of Magnesium-oxide. This light possesses many actinic rays, and is used in photography as a flash-light.

It readily dissolves in acids, evolving Hydrogen.

Magnesium comes on the market in ribbon form and as a powder. It is found in large quantities in nature as *magnesite*, (Magnesium-carbonate) and *dolomite* (a mixture of Magnesium carbonate and Calcium-carbonate). It is further found as a silicate in talcum, meerschaum, asbestos, soapstone, etc.

Metallic Magnesium is prepared by melting Magnesium-chloride with metallic Sodium:

$$MgCl_2 + 2Na = Mg + 2NaCl$$

The metal is then purified by distillation.

Magnesium-sulphate (Magnesii sulphas) $MgSO_4$

Also known as *Epsom salts*. Contains 7 molecules of water of crystallisation ($MgSO_4$,7aq.). It is efflorescent and soluble in water, where it has a neutral reaction. It acts as a laxative, and is of a bitter, salty taste. It is contained in the waters of certain springs at Epsom, in England; but is largely prepared by dissolving Magnesium-carbonate in sulphuric acid:

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2$$

Magnesium-chloride (Magnesii chloridum), $MgCl_2$

White, deliquescent salt, prepared by dissolving Magnesium-carbonate in hydrochloric acid.

Magnesium-carbonate (Magnesii carbonas), $MgCO_3$

Found in nature as magnesite and dolomite, but these are not chemically pure. For pharmaceutical purposes it is prepared by precipitating a solution of Magnesium-sulphate with one

of Sodium-carbonate. It is a white powder, insoluble in water, and very light; it is called *magnesia alba* and *light Magnesium-carbonate.* If the solutions, when mixed, are evaporated, the residue washed, filtered and dried, the product is heavier and is called *heavy Magnesium-carbonate.* The official preparation is the Magnesium-sub-carbonate, and should be written:

$$4MgCO_3 + Mg(OH)_2 + 5H_2O$$

Magnesium-oxide (Magnesii oxidum), MgO

Also called *magnesia,* and *calcined magnesia.* Prepared by heating Magnesium-carbonate; CO_2 escapes, and the oxide is left. There are two forms of the oxide official: light magnesia or magnesia (*Magnesii oxidum*), prepared from the light carbonate; and the heavy magnesia(*Magnesii oxidum ponderosum*), prepared from the heavy carbonate.

Magnesium-oxide is a light, white powder, insoluble in water; but water gradually changes it into the gelatinous hydroxide, $Mg(OH)_2$, which is also almost insoluble. It should be kept well closed, for if in contact with air it absorbs Carbon-dioxide and forms Magnesium-carbonate.

Test for Magnesium: The addition of Ammonium-chloride, Sodium-phosphate and ammonia-water gives a white crystalline precipitate, which is a double salt of Magnesium-phosphate and Ammonium-phosphate, $MgNH_4.PO_4$.

CALCIUM.

SYMBOL, Ca; AT. MASS, 39.8; VALENCE, II.

Metallic Calcium is of no importance, but forms important compounds. It occurs most commonly in nature as 1, Calcium-carbonate, which is known as calcite, marble, chalk, limestone —differing only in hardness and structure. 2, as Calcium-sulphate, in a mineral commonly called *gypsum* or *alabaster.* 3, as Calcium-phosphate: in the bones of animals, and in the mineral *apatite.*

Calcium-chloride (*Calcii chloridum*), $CaCl_2$

In crystalline condition, it consists of colorless, deliquescent prisms, easily soluble in water, and containing water of crystallisation. It melts on being heated, and becomes anhydrous at 200°. This is the official salt. It is white, very soluble in water, and deliquescent. It is used for drying purposes, especially for drying gases, which are passed through tubes containing small pieces of it (*Calcium-chloride tubes*). It is prepared by treating chalk or marble (Calcium-carbonate) with hydrochloric acid. The solution obtained is filtered, evaporated to dryness, and the residue heated to 200° C.

Fused Calcium-chloride is the solid mass obtained by heating to red heat, and then allowing to cool.

Calcium-bromide (*Calcii bromidum*), $CaBr_2$

White salt, soluble in water and very deliquescent. Prepared by dissolving Calcium-carbonate in hydrobromic acid.

Calcium-carbonate (*Calcii carbonas*), $CaCO_3$

Found in nature as marble, limestone, chalk, calcite, etc. None of these are chemicallly pure, unless it be the crystallised calcite. Crude powdered chalk is sold under the name of *whiting*. It is official as precipitated Calcium-carbonate (*Calcii carbonas praecipitatus*, a fine, white powder, without taste or smell, insoluble in water. It is prepared as follows: Chalk is dissolved in hydrochloric acid, forming a solution of Calcium-chloride. All sand and impurities are removed from this solution, as nearly as possible, by filtering. It still contains a little Iron, however, and this should be removed by oxidising it to the Ferric condition by treating the solution with Chlorine and then ammonia-water, when the Iron is precipitated as Ferric hydrate. A solution of the pure Calcium-chloride is mixed with a solution of Sodium-carbonate, and a white precipitate of Calcium-carbonate results, which is washed and dried.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

Calcium-oxide (Calcii oxidum), CaO

Known as *lime, (Calx), quick-lime, burnt lime.* Prepared by heating Calcium-carbonate in limekilns, where it is decomposed into Calcium-oxide and Carbon-dioxide, which latter passes off as a gas. This is the process of *calcination.*

Lime consists of hard lumps, which will take up Carbon-dioxide from the air and form Calcium-carbonate on exposure. When water is added to lime, it generates heat and falls into a white powder, *slaked lime.* This is a compound of lime with water:

$$CaO + H_2O = Ca(OH)_2$$

and this is Calcium-hydroxide. The best way to slake lime is to dip a piece of it into cold water for a half-minute, and then take out of the water, and let stand in a loosely-covered jar for about 30 minutes. It is converted into a white powder.

Calcium-hydroxide (Calcii hydroxidum), $Ca(OH)_2$

Commonly called *slaked lime,* as it is made by slaking lime with water. It is a white powder, somewhat soluble in water—more in cold than in hot. A cold saturated solution containing 0.17 percent is official as *lime water (liquor Calcis).* This is a colorless liquid, and on being heated it becomes cloudy, the lime, being less soluble and separating out in the hot solution. Lime-water has an alkaline reaction. It must be kept away from contact with air, or it will take up CO_2 and form Calcium-carbonate, which forms a white precipitate on the walls of the container. Lime is much more soluble in water if sugar is also present, for the two unite chemically.

An aqueous mixture containing more lime than the water can dissolve, has the appearance of milk and is called *milk of lime.*

Calcium-sulphate (Calcii sulphas), $CaSO_4$

Found in nature (containing water of crystallisation) in several minerals, as in gypsum, alabaster, etc. Gypsum is a white solid, and when heated it loses its water of crystallisation and falls into a white powder, called *plaster of Paris.* This powder combines with water slowly and solidifies.

It is official under the name *Calcii sulphas exsiccatus.*

Calcium-phosphate (*Calcii phosphas*), $Ca_3(PO_4)_2$

A white substance, insoluble in water, found in the bones of animals, from which it is obtained by burning until the bones are white. This product is called *bone-ash,* and is crude Calcium-phosphate. *Apatite* and some other minerals also contain Calcium-phosphate.

For pharmaceutical use it is prepared by precipitating a solution of Calcium-chloride with one of Sodium-phosphate—adding at the same time some ammonia

$$2Na_2HPO_4 + 3CaCl_2 + 2NH_4OH = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl + 2H_2O$$

The official form (*Calcii phosphas praecipitatus*) is a white powder without taste or smell, insoluble in water.

Calcium-sulphide (*Calx sulphurata*), *CaS*

A grayish-white substance, almost insoluble in water, having an alkaline, nauseating taste, and a faint smell of Hydrogen-sulphide. If treated with an acid, Hydrogen-sulphide is evolved. If previously exposed to sunlight, Calcium-sulphide will emit light in a dark room. The official chemical is not pure, but is mixed with some Calcium-sulphate and some Carbon.

It should contain 60 percent of Calcium-sulphide, and is prepared by mixing plaster of Paris with some coal and starch, adding water to solidify, and glowing in a furnace:

$$CaSO_4 + 2C = CaS + 2CO_2$$

Chlorinated lime, Chloride of lime (*Calx chlorata*)

Also called *bleaching powder;* a white, deliquescent powder having an odor of Chlorine. It is considered as a mixture of Calcium-chloride, Calcium-hypochlorite, and some Calcium-hydroxide—the latter giving the solution an alkaline reaction. It is only partially soluble in water. If treated with an acid, all Chlorine is liberated; it should contain 30 percent available Chlorine. It is prepared by passing Chlorine gas over slaked lime. See Hypochlorous acid.

Calcium-hypophosphite (Calcii hypophosphis), $Ca(H_2PO_2)_2$

A white, granular powder, easily soluble in water. On being heated in the dry state, it forms Calcium-phosphate, at the same time yielding a self-inflammable phosphine. It is prepared by boiling Phosphorus, slaked lime, and water together; phosphine gas escapes, and Calcium-hypophosphite goes into solution. This solution is filtered, the excess of Calcium-hydroxide precipitated as carbonate by passing Carbon-dioxide through the solution, which is then again filtered, and evaporated.

Tests for Calcium. 1, Add to the solution to be tested aqua ammonia, then Ammonium-oxalate. If Calcium is present, a white precipitate of Calcium-oxalate is obtained, which is insoluble in ammonia water and in acetic acid. 2, Ammonium-carbonate gives a white precipitate of Calcium-carbonate. 3, Sulphuric acid or soluble sulphate gives a white precipitate of Calcium-sulphate, if the solution be not too much diluted.

STRONTIUM.

SYMBOL, Sr; AT. MASS, 86.94; VALENCE, II.

Strontium is of no importance in the metallic condition, but its compounds are important. They are white unless the acid colors them, and impart a beautiful red color to the flame.

Strontium is found in nature as *strontianite,* Strontium-carbonate, and as *celestite,* Strontium-sulphate.

The salts are prepared from the carbonate by dissolving it in the acid; or from the sulphate by heating it with coal to convert it into the sulphide, and then dissolving in acids.

Strontium-nitrate (Strontii nitras), $Sr(NO_3)_2$

White salt, soluble in water. Prepared by treating Strontium-carbonate with nitric acid. Used for red fire.

Strontium-carbonate (Strontii carbonas), $SrCO_3$

White substance, insoluble in water. Occurs naturally as strontianite.

Strontium-oxide (*Strontii oxidum*), *SrO*

Resembles lime closely; slakes with water, forming Strontium-hydroxide, $Sr(OH)_2$, which is more soluble than Calcium-hydroxide. Prepared by heating Strontium-nitrate.

Strontium-chloride (*Strontii chloridum*), $SrCl_2$

White, deliquescent substance, soluble in water. Prepared by treating Strontium-carbonate with hydrochloric acid.

Strontium-bromide (*Strontii bromidum*), $SrBr_2$

White, deliquescent salt, soluble in water. Prepared by treating Strontium-carbonate with hydrobromic acid.

Strontium-iodide (*Strontii iodidum*), SrI_2

White, deliquescent salt, soluble in water. Prepared by treating Strontium-carbonate with hydriodic acid.

Tests for Strontium: 1, With sulphuric acid or soluble sulphate it forms a white precipitate of Strontium-sulphate. 2, It colors the flame red. 3, With Ammonium-carbonate, it gives a white precipitate of Strontium-carbonate.

BARIUM.

SYMBOL, Ba; AT. MASS, 136.4; VALENCE, II.

Barium is found in nature as *witherite*, Barium-carbonate, and as *heavy spar*, Barium-sulphate. Its compounds are white, unless the acid colors them, and are very heavy (the name of the metal is derived from the greek word for heavy). They impart a green color to the flame, and are used in making 'green fire.' All are poisonous. Their preparation is the same as the compounds of Strontium.

Barium-carbonate (*Barii carbonas*), $BaCO_3$

White mineral, occurring in nature as witherite. Insoluble in water.

Barium-oxide (*Barii oxidum*), *BaO*

Also called *baryta,* and is analagous to lime. It is obtained by heating Barium-nitrate. It should be kept in well-stoppered bottles, as it absorbs Carbon-dioxide from the air and forms the carbonate. If treated with water, it slakes and forms the hydroxide, $Ba(OH)_2$.

Barium-hydroxide (*Barii hydroxidum*), $Ba(OH)_2$

This is best prepared by adding Barium-chloride to a boiling (15 percent) solution of Sodium-hydroxide:

$$BaCl_2 + 2NaOH = Ba(OH)_2 + 2NaCl$$

On cooling, the Barium-hydroxide crystallises out, with water of crystallisation. It is much more soluble in water than is Calcium-hydroxide, and an aqueous solution is used in chemistry under the name 'baryta-water' (*liquor barytae*). This resembles lime-water, and, if exposed to air, forms a precipitate of Barium-carbonate.

Barium-dioxide (*Barii dioxidum*), BaO_2

A grayish-white powder, almost insoluble in water. It can be obtained by heating Barium-oxide, BaO, in a current of air or Oxygen. If further heated, the dioxide gives up the Oxygen and is therefore a good oxidising agent. When Barium-dioxide is heated with hydrochloric acid, it forms free chlorine; if treated with sulphuric or phosphoric acid, it forms Hydrogen-dioxide.

It is employed to prepare Oxygen cheaply. The Barium-dioxide is heated, and splits up into Oxygen (which is collected in tanks) and the oxide, BaO. When the latter is somewhat cooled and placed in a current of air, it takes up Oxygen and again becomes the dioxide.

Barium-nitrate (*Barii nitras*), $Ba(NO_3)_2$

White crystals, soluble in water, prepared by dissolving Barium-carbonate in nitric acid. Used for 'green fire.'

Barium-chloride (*Barii chloridum*), $BaCl_2$

White salt, soluble in water, prepared by dissolving Barium-

carbonate in hydrochloric acid. Used as a test for sulphuric acid.

Tests for Barium: With sulphuric acid or a soluble sulphate, it gives a white precipitate. 2, It colors the flame green. 3, With Ammonium-carbonate it gives a white precipitate of Barium-carbonate. 4, With Potassium-chromate it gives a yellow precipititate of Barium-chromate, insoluble in acetic acid.

GLUCINUM or BERYLLIUM.

SYMBOL, Gl *or* Be; AT. MASS, 9.03; VALENCE, II.

This is a rare element, and occurs native in the mineral *Beryl*, which is a double silicate of Aluminum and Beryllium. It is also found as the precious stone *emerald*, which is colored green by the presence of a Chromium salt. Beryllium resembles Magnesium closely. Its salts are colorless, and have a sweetish taste, which accounts for the name Glucinum.

RADIUM.

SYMBOL, Ra; AT. MASS, 223; VALENCE, II.

In 1896, Becquerel discovered that Uranium and its compounds, when brought near to a photographic plate entirely surrounded with black paper, will affect it. The rays which are thus able to pass through the intervening air and then through the black paper are known as *Becquerel rays*.

It was further found that air, which is not normally an electrical conductor, becomes one under the influence of these rays.

Thorium and its compounds also emit Becquerel rays, and they, together with the previously mentioned bodies, are said to possess *radio activity*. The unit of radio activity is the magnitude contained in metallic Uranium.

The mineral *pitchblende* is the principal source of Uranium, and this compound shows radio activity.

Mr. and Mrs. Currie, of Paris, found in their investigations that when all the known constituents of pitchblende are removed

by crystallisation, etc., the radio activity of the residue is increased. They concluded that some one unknown constituent possessed this wonderful activity, and they eventually succeeded in isolating this element, and called it *Radium*.

Polonium and *Actinium* have also been isolated, but have been little studied as yet.

Radium belongs to the alkali-earth metals, and its properties are similar to those of Barium—except for the remarkable radio activity which it possesses. This activity is more than 1¾ million millions times as much as the magnitude of the radio activity of Uranium. Its compounds possess this power, and Radium-chloride ($RaCl_2$) and Radium-bromide ($RaBr_2$) are used in experiments.

Radium has the following properties: 1, Its temperature is always higher than the surrounding air—it is capable of melting its own weight of ice every hour. 2, It is luminous in the dark. 3, It imparts to other bodies (diamond, Zinc-sulphide, Barium-Platino-cyanide) which have been for some time in its vicinity, this property of luminosity, which they retain for a considerable period of time after the removal of the Radium. 4, It affects the photographic plate, and emits rays similar to Rontgen rays. 5, It renders air a conductor of electricity. 6, It has the property of making itself apparent even if it be enclosed in a wooden box and the observer's eyes are closed—the blind are aware of its proximity. 7, If kept near the person, though in closed tubes, it produces painful skin-sores, which heal slowly. 8, It kills outright, or lessens the vitality of, lower organisms and plants with which its rays come in contact.

The original observations on Radium seemed to show that this radio activity did not become lessened: a fact entirely at variance with the all-important law of the conservation of energy. Recent investigations, however, have shown that this is not the case, and that it suffers a diminution of these powers.

According to the theory of Crookes, a radio active substance permanently discharges particles, as the *emanation of Radium*.

This emanation is supposed to be *the fourth state of matter.* or *radiant matter.*

There are two kinds of these particles:

1. *Real atoms;* that is, chemical atoms. They are relatively large, and charged with positive electricity. These cause the air to become a conductor, and act upon the photographic plate. They are prevented by collision with other bodies from continuing their lines of motion.

2. *Electrons.* These are far smaller than chemical atoms. which are no longer considered as the ultimate divisions of matter, except in the chemical sense. Each atom contains a great number of electrons, which are usually there in a state of stable *equilibrium,* causing the atom to be stable. In some instances, however (as in Radium and other radio active bodies), the particles which form the chemical atom are only banded together in a very unstable condition. By virtue of their position in the atom they possess potential energy, which is gradually converted into kinetic energy, causing the atoms to tend to split up into *electrons.* These are thrown off with enormous velocity, bombarding the bodies within their vicinity. Some of the particles adhere to these extraneous bodies, which thus in turn 'borrow' a measure of radio activity.

By this conversion of potential energy stored up in the enforced positions of the particles in the atoms, heat, electricity, light, etc., are produced.

The particles will gradually assume more stable positions in the atoms, and this will result in the transformation of one kind of atom into another—the transformation of one element into another. It has been proven that Radium emanations contain Helium, hence a gradual change of Radium into Helium (and possibly other elements) takes place.

Group II—Family B.

This group contains metals which are more distantly related to the alkali-earth metals: they are Zinc, Cadmium and Mercury.

ZINC.

SYMBOL, Zn; AT. MASS, 64.9; VALENCE, II.

Zinc is a Silver-white metal, somewhat crystalline. It is readily fusible, and, under sufficient heat, distils. If heated in air, it ignites and burns with a bluish flame to form Zinc-oxide. It is soluble in dilute acids, its solution in them being accompanied by the evolution of Hydrogen.

It is found native as *calamine,* Zinc-carbonate, *Zincblende,* Zinc-sulphide, and as Zinc-silicate. It is prepared from these ores as follows: They are reduced to the oxide by heating or roasting as the case may be; the Zinc-oxide is then reduced to the metallic state by distillation with Carbon. A gray powder collects in the retort, and this is called *Zinc-dust.* It is a mixture of metallic Zinc and Zinc-oxide. Later, the liquid Zinc distils over. Zinc compounds are white.

Zinc-sulphate (Zinci sulphas), $ZnSO_4$

Also called *white vitrol.* Cantains 7 molecules of water of crystallisation and is efflorescent. It is isomerous with Epsom salt, but has an acid reaction. Prepared by dissolving the metal in dilute sulphuric acid; Hydrogen is evolved.

Zinc-chloride (Zinci chloridum), $ZnCl_2$

White, deliquescent mass, easily soluble in water. Official as the solid mass, and as a 50 percent solution (*liquor Zinci chloridi*). This salt is markedly caustic. Prepared by dissolving metallic Zinc in hydrochloric acid (Hydrogen escapes).

Zinc-bromide (Zinci bromidum), $ZnBr_2$

White, deliquescent powder, soluble in water. Prepared by treating metallic Zinc with water and Bromine.

Zinc-iodide (Zinci iodidum), ZnI_2

White, deliquescent substance, soluble in water. Prepared by treating metallic Zinc with water and Iodine.

Zinc-oxide (Zinci oxidum), ZnO

White powder, insoluble in water. Should be kept in well-closed bottles, as it takes up CO_2 from air and forms the carbonate. Used in large quantities in paints as *Zinc-white.* Prepared by burning metallic Zinc, or heating Zinc-carbonate:

$$ZnCO_3 = ZnO + CO_2$$

When heated, it acquires a yellow color which disappears on cooling.

Zinc-carbonate (Zinci carbonas), $ZnCO_3$

White powder, insoluble in water. It is really a basic salt. Prepared by mixing a solution of zinc sulphate with one of Sodium-carbonate. The Zinc-carbonate precipitates.

$$ZnSO_4 + Na_2CO_3 = ZnCO_3 + Na_2SO_4$$

Tests for Zinc: 1, With Hydrogen-sulphide, in alkaline solution, it gives a white precipitate. 2, When treated with a solution of Potassium-ferrocyanide, it gives a white precipitate of Zinc-ferrocyanide. 3, With Potassium-hydroxide, it forms a precipitate soluble in excess of the alkali.

CADMIUM.

SYMBOL, Cd; AT. MASS, 111.6; VALENCE, II.

This metal is frequently found in Zinc ores, and commercial Zinc often contains Cadmium. It is more volatile than Zinc, and the two can be separated by fractional distillation. Cadmium resembles Zinc closely.

Cadmium-oxide (Cadmii oxidum), CdO

A brown powder, insoluble in water.

Cadmium-sulphide (Cadmii sulphidum), CdS

A yellow powder, insoluble in water. Formed when Hydrogen-sulphide is passed through a solution of Cadmium.

Cadmium-hydroxide (*Cadmii hydroxidum*), $Cd(OH)_2$

A white powder, obtained by precipitating a Cadmium salt with an alkali. Readily soluble in ammonia-water.

The Cadmium salts are colorless.

MERCURY (Hydrargyrum).

SYMBOL, Hg; AT. MASS, 198.5; VALENCE, (I) II

Mercury is often called *quicksilver*. At ordinary temperatures it is a Silver-white liquid having a specific gravity of 13.6. It freezes and solidifies at —39° C., and boils at 357° C.; but it vaporises even at ordinary temperature and evolves poisonous vapors. Metallic Mercury dissolves other metals, and combines with them to form *amalgams*. Gold, dissolved in Mercury, forms Gold-amalgam. Mercury stains on Gold and other metals may be removed by heating the stained body over a non-luminous flame for a short time—this vaporises the Mercury. A few metals do not form amalgams with Mercury, for instance Iron. Iron containers are used for shipping Mercury.

Metallic Mercury enters into five galenical preparations:

Mercurial ointment (*unguentum Hydrargyri*), 50 percent.
Blue ointment (*unguentum Hydrargyri dilutum*),
Mercury with chalk (*Hydrargyrum cum creta*), 38 *percent.*
Blue mass (*massa Hydrargyri*), 33 percent.
Mercurial plaster (*emplastrum Hydrargyri*), 30 percent.

If Mercury is triturated for a long time with powder, ointment or oil, it changes into very small drops which cannot be distinguished with the naked eye nor with a low-power lens. The general appearance of the substance with which it is mixed is still the same—powder, ointment, or oil. This is the process of *killing* or *extinguishing* Mercury, and must be performed before Mercury is used in pharmaceutical preparations.

Mercury is soluble in some acids. It is soluble in boiling sulphuric acid, Sulphur-dioxide escaping during solution.

Nitric acid dissolves it, and Nitrogen-dioxide is liberated. If an excess of Mercury is dissolved in cold nitric acid, Mercurous-nitrate results; but if nitric acid is in excess and the solution be boiled, Mercuric-nitrate results.

Mercury forms two classes of compounds, Mercurous and Mercuric.

In Mercurous compounds, Mercury is univalent; in Mercuric it is divalent. Therefore, Mercurous compounds contain a larger amount of Mercury.

Mercury compounds, on being heated, volatilise. They are poisonous, their virulence increasing with their solubility.

Mercurous-chloride contains more Mercury than Mercuric-chloride, but is less poisonous because less soluble. Mercurous compounds must be kept away from direct light, as on exposure they break down into metallic Mercury and the Mercuric salt. They also become darker, by reason of the metallic Mercury present:

$$Hg_2I_2 = HgI_2 + Hg$$

Most of the Mercury compounds are white or colorless; those with color are oxides, sulphides, iodides, and some subsalts.

Mercury is found in the metallic state sprinkled through different minerals, and it is obtained from these by crushing them and subjecting them to distillation. It is further found as sulphide in a red ore called *cinnabar,* and is prepared by burning this; the Sulphur-dioxide formed escapes, and the oxide of Mercury, which is unstable at high temperatures, frees its Mercury.

It is also obtained by distilling cinnabar with metallic Iron.

It occurs most frequently in the U. S., Spain and Austria.

Mercurous-nitrate ($HgNO_3$)

A white salt, soluble in water containing some acid; pure water decomposes it into an insoluble basic salt. It is obtained by dissolving an excess of Mercury in cold nitric acid.

Mercuric-nitrate (*Hydrargyri nitras*), $Hg(NO_3)_2$

A white salt, soluble in water containing free acid; pure

water decomposes it into a basic nitrate. It is prepared by dissolving Mercury in an excess of nitric acid. It is official in a 60 percent solution, under the name of *liquor Hydrargyri nitratis.* This is prepared by dissolving oxide of Mercury in nitric acid.

Mercurous-sulphate (Hg_2SO_4)

A white salt of no importance.

Mercuric-sulphate (*Hydrargyri sulphas*), $HgSO_4$

Sometimes called *bisulphate of Mercury,* and used in electric batteries. Prepared by boiling Mercury with sulphuric acid, Sulphur-dioxide escaping:

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$$

To hasten solution, it is advisable to add some nitric acid. It is a white salt, soluble in water containing free acid. If a large amount of pure water is present, the salt is decomposed and forms a bright-yellow precipitate, which is Mercury-subsulphate.

Mercuric-subsulphate (*Hydrargyri subsulphas flavus*), $HgSO_4 + 2HgO$

This may be considered as a compound of Mercuric-sulphate with Mercuric-oxide. It is a yellow powder, tasteless and insoluble in water. It acts as an emetic and an errhine. It is known as *turpeth mineral,* and is prepared by dissolving Mercury in a mixture of sulphuric and nitric acids; Mercuric-sulphate is formed, and this is evaporated to dryness and an excess of water added.

Mercuric-chloride (*Hydrargyri bichloridum corrosivum*), $HgCl_2$

Also known as *corrosive sublimate,* is a white, heavy salt, soluble in water (1:13) and more so in alcohol. The addition of a soluble chloride renders it more soluble in water, a double salt being formed. For this reason, corrosive sublimate tablets contain some Ammonium-chloride. It is a powerful antiseptic, and is prepared by sublimation of a mixture of Mercuric-sulphate and Sodium-chloride.

Mercurous-chloride (Hydrargyri chloridum mite) HgCl

Commonly called *calomel,* a white, heavy powder, insoluble in water or alcohol. On being heated, it sublimes without fusion. Chlorine or oxidising agents change it into corrosive sublimate. Hydrochloric acid and soluble chlorides convert it slowly into Mercurous-chloride and metallic Mercury.

$$2HgCl = HgCl_2 + Hg$$

It is prepared

1, By sublimation of a mixture of metallic Mercury and Mercuric-chloride:

$$HgCl_2 + Hg = 2HgCl$$

The sublimate formed is then triturated with water until a very fine powder is obtained. This is washed to free it from all Mercuric-chloride. Calomel prepared in this manner is fit for internal medication.

2, Sometimes, the vapors of the subliming calomel are passed into rooms into which jets of steam also enter. Calomel treated in this manner forms a much finer powder than is obtainable by the first method. It is more poisonous, however, and should not be used internally; it may be used for external application.

3, Calomel can be obtained by precipitating a Mercurous-nitrate solution with a solution of hydrochloric acid or Sodium-chloride.

$$HgNO_3 + NaCl = HgCl + NaNO_3$$

Mercuric-iodide (Hydrargyri iodidum), HgI_2

Also called *red iodide of Mercury (Hydrargyri iodidum rubrum)* and *biniodide of Mercury.* It is a scarlet-red powder, insoluble in water, but soluble in alcohol and in water containing Potassium-iodide. Here it forms a double salt of Mercuric-Potassium-iodide ($HgI_2 + KI + 1\frac{1}{2}H_2O$). Its solutions are colorless. It is prepared: 1, by precipitating a solution of corrosive sublimate with one of Potassium-iodide:

$$HgCl_2 + 2KI = HgI_2 + 2KCl$$

An excess of Potassium-iodide must be avoided, or it will dissolve the precipitate of Mercuric-iodide.

2. By triturating Iodine and metallic Mercury in the proper proportions—adding alcohol from time to time.

Mercurous-iodide (*Hydrargyri iodidum flavum*), *HgI*

A yellow powder, insoluble in water and alcohol; also called *yellow iodide of Mercury,* or *Mercury-prot-iodide.* It is decomposed by light into Mercuric-iodide and metallic Mercury, the latter lending to it a greenish tint. According to the U. S. P., it should be prepared by dissolving metallic Mercury in cold nitric acid (Mercury being in excess). A solution of Mercurous-nitrate is thus obtained, and this is mixed with a solution of Potassium-iodide, causing Mercurous-iodide to precipitate:

$$HgNO_3 + KI = HgI + KNO_3$$

The precipitate is washed with alcohol to free it from all red iodide of Mercury.

2, By triturating metallic Mercury and Iodine together in the proper proportions, adding alcohol from time to time.

Mercurous-oxide (Hg_2O)

A black powder, insoluble in water. Prepared by treating a solution of a Mercurous salt with a solution of Potassium-hydroxide. It is present in *black wash* or *lotio nigra.* This contains calomel and lime-water, which form Calcium-chloride and Mercurous-oxide.

Mercuric-oxide (*Hydrargyri oxidum*), *HgO*

Occurs in two modifications, the red and the yellow. They are chemically the same, but differ physically. Besides differing in color, the yellow oxide is made up of finer grains than the more coarse red oxide. The variation is caused by different methods of preparation.

Red oxide of Mercury (*Hydrargyri oxidum rubrum*), *HgO*

A red, heavy, rather coarse powder, which is insoluble in water, alcohol, etc. It is sometimes called *red precipitate,* although not made by precipitation. It is prepared by heating Mercuric-nitrate.

Yellow oxide of Mercury (*Hydrargyri oxidum flavum*), *HgO*

A fine, yellow powder, insoluble in water. Prepared by precipi-

tating a solution of corrosive sublimate with one of Potassium-hydroxide

$$HgCl_2 + 2KOH = HgO + 2KCl + H_2O$$

The Mercuric-hydroxide, which might be supposed to precipitate by this process, is not known; we assume that it decomposes at once into the oxide and water.

This variety being subdivided to a much finer condition than the red form, is more easily acted upon by acids. If treated with a solution of oxalic acid, it is converted into white oxide of Mercury in 15 minutes, while the red oxide resists this conversion for two hours. The yellow oxide is also more energetic in its medical action. It is present in *yellow wash* or *lotio flava.* This consists of corrosive sublimate and lime-water, which form Mercuric-oxide and Calcium-chloride.

If either oxide of Mercury is heated, it becomes black, but changes to red on cooling. If further heated, it is decomposed into metallic Mercury and Oxygen.

Ammoniated Mercury (Hydrargyrum ammoniatum), NH_2HgCl

Known also as *white precipitate.* It may be considered as Ammonium-chloride (NH_4Cl), in which two Hydrogen atoms are replaced by one bivalent Mercury atom. It is a white substance, insoluble in water, but soluble in acids. When heated, it evaporates without first fusing. It is prepared by precipitating a solution of corrosive sublimate with ammonia:

$$HgCl_2 + 2NH_4OH = NH_4Cl + NH_2HgCl + 2H_2O$$

Mercuric-sulphide (Hydrargyri sulphidum), HgS

This compound occurs in two modifications:

1. *Crystalline.* Beautiful red crystalline masses, occurring native as *cinnabar* or *vermillion.* It is insoluble in water and dilute acids, but readily soluble in a mixture of nitric and hydrochloric acids. It is employed in paints.

2. *Amorphous.* A black powder, insoluble in water and dilute acids, but soluble in a mixture of nitric and hydro-

chloric acids. It is formed when Hydrogen-sulphide is passed through a solution of a Mercuric salt. When sublimed, it cools as the crystalline form.

Tests for Mercury (for all salts): 1, With Hydrogen-sulphide a black precipitate is formed in any solution. 2, A solution of any Mercury-salt will impart a silvery stain to a clean piece of Copper. This disappears on heating. 3, Stannous-chloride gives a white or gray precipitate. If white, the precipitate is Mercurous-chloride; if gray, metallic Mercury.

Tests for Mercuric salts only: 1, A solution of Mercuric compound forms with Potassium-hydroxide a yellow precipitate of Mercuric-oxide. 2, Ammonia-water gives a white precipitate.

Tests for Mercurous salts only: Potassium- or Ammonium-hydroxide produces a black precipitate. 2, Hydrochloric acid or other soluble chloride yield a white precipitate.

Group III.

The elements of the third group have the oxide formula E_2O_3, and the valence of 3. There are two families:

Family A—the elements of the even series of the long periods: Scandium, Yttrium, Lanthanum and Ytterbium. They are contained in some of the rarer minerals, together with Cerium and Erbium. They are of no importance.

Family B—the elements of the short periods and the elements of the odd series of the long periods of the third group. They are: Boron, Aluminum, Gallium, Indium and Thallium. Boron has been studied with the non-metals; the principal of the remaining elements of the group is

ALUMINUM.

SYMBOL, Al; AT. MASS, 26.9; VALENCE, III.

Aluminum is a Silver-white, light metal, capable of taking a high polish. Its specific gravity is about 2.7. It is soft, but tough and resistant. Oxygen does not readily unite with it, and it therefore keeps bright in air. It is little affected by nitric acid, but readily by hydrochloric acid.

Aluminum is of frequent occurrence in nature as feldspar, emery, cryolite and clay; and is often called *silver from clay*. It is present in some precious stones, as in the ruby, saphire, corundum. Clay is principally Aluminum-silicate. The finer grade of clay used for making porcelain is called *kaolin* or *porcelain clay*. Aluminum, like Iron in the Ferric condition, does not combine with carbonic acid nor form a carbonate.

Aluminum is prepared by melting Aluminum-chloride with metallic Sodium. The Chlorine combines with the Sodium, leaving the free Aluminum. It may also be obtained by passing an electric current through molten Aluminum-fluoride or the

double salt of Aluminum- and Sodium- fluoride found native. The Aluminum salts are colorless unless the acid colors them.

Aluminum-sulphate (*Alumini sulphas*), $Al_2(SO_4)_3$.

White crystals, soluble in water, of a sour and astringent taste. They contain water of crystallisation. Prepared by treating clay with sulphuric acid, filtering, and evaporating the solution to crystallisation. It may be obtained in a purer condition by treating Aluminum-hydroxide with sulphuric acid.

Aluminum-sulphate is characterised by its ability to unite with the sulphates of the alkali-metals and form double salts, called *alums*. All the different varieties of alums are isomorphous, and crystallise in octahedrons; all contain water of crystallisation. Alums may also be formed by the sulphates of other trivalent elements (Iron, Manganese, Chromium) in combination with alkali-sulphates.

Alums contain two molecules of sulphuric acid, of which three Hydrogen atoms are replaced by a tri-valent element, the fourth by a univalent alkali-metal, as follows:

Aluminum-Potassium alum, $AlK(SO_4)_2 + 12H_2O$
Aluminum-Sodium alum, $AlNa(SO_4)_2 + 12H_2O$
Aluminum-Ammonium alum, $AlNH_4(SO_4)_2 + 12H_2O$
Iron-Potassium alum, $FeK(SO_4)_2 + 12H_2O$
Iron-Ammonium alum, $FeNH_4(SO_4)_2 + 12H_2O$
Manganese-Potassium alum, $MnK(SO_4)_2 + 12H_2O$
Chromium-Potassium alum, $CrK(SO_4)_2 + 12H_2O$

The most important one is the Aluminum-Potassium alum, usually called *alum* (*alumen*). This occurs as white crystals, soluble in water, of a sour and astringent taste and acid reaction. Much used in dyeing industry as a mordant—to make the color 'fast.' It is neither efflorescent nor deliquescent. It is official in two forms as the crystals, and as *burnt alum* (*alumen exsiccatum*). The latter is prepared by powdering the alum, and heating it on a sand-bath.

Common alum is usually prepared by treating clay with sulphuric acid, forming Aluminum-sulphate; this solution is fil-

tered, mixed with a solution of Potassium-sulphate, and the mixture crystallised. Basic alum is found in nature as *alunite.*

Aluminum-hydroxide (Alumini hydroxidum), $Al(OH)_3$

A white, gelatinous substance, insoluble in water, soluble in acids and in a solution of Potassium-hydroxide. It has acid as well as basic properties, and when treated with fixed alkalies (Sodium-hydroxide, Potassium-hydroxide) it dissolves and forms salts, the *aluminates.* The formula of Potassium-aluminate is K_3AlO_3. It does not unite with weak acids like carbonic acid. If a solution of an Aluminum salt is mixed with a solution of a carbonate, the precipitate formed is not Aluminum-carbonate but Aluminum-hydroxide—Carbon-dioxide escaping during the reaction.

Aluminum-hydroxide is able to combine with organic coloring matters if brought together with them in solution. Precipitates are thus formed which are called *lakes.* For this reason, the Aluminum salts are used in dying, to precipitate the colors in the fibers of the goods.

Aluminum-hydroxide can be prepared by precipitating a solution of Aluminum-sulphate with ammonia-water. The U. S. P. uses Sodium-carbonate for the precipitation.

Ultra Marine

A blue powder, insoluble in water. Treated with acids, it generates Hydrogen-sulphide, and therefore contains a sulphide. It is much used in painting, and is found natural as *lapis lazuli.* A green variety also exists. Its chemical constitution is not yet known. It is made artificially by heating a mixture of clay, Sulphur, Sodium-sulphate, Sodium-carbonate and coal.

Tests for Aluminum: 1, Ammonia-water forms a white, voluminous precipitate, soluble in Potassium-hydroxide. Potassium-hydroxide and Sodium-hydroxide give a similar precipitate, but this redissolves in an excess of these hydroxides.

2, Sodium-phosphate gives a white precipitate of Aluminum-phosphate, which is soluble in acids and in fixed alkalies.

Rarer Metals of Group III—Family B

GALLIUM.

SYMBOL, Ga; AT. MASS, 69.5; VALENCE, III.

This is a rare element, the existence of which was predicted by Mendeljeff from the periodic law arrangement, and later discovered by Lecoq de Boisbaudran by means of the spectroscope. It is a white, hard metal, easily fusible (melting point, 30° C.). Its salts are colorless.

INDIUM.

SYMBOL, In; AT. MASS, 113.1; VALENCE, III.

Discovered by Reich and Richter by means of the spectroscope. The spectrum shows a bright indigo-blue line, hence the name. It is not important.

THALLIUM.

SYMBOL, Tl; AT. MASS, 202.6; VALENCE, I, III.

Crookes discovered it by the aid of the spectroscope, and it was named on account of its characteristic green lines. It frequently occurs in Iron pyrites and in Zinc blendes, but always in small quantities.

Thallium is a soft but tough metal, and leaves a streak on paper if rubbed over it. It readily oxidises. It forms Thallous compounds, and Thallic compounds. The former resemble closely the compounds of the alkali-metals. Thallous-hydroxide and Thallous-carbonate are soluble in water and strongly alkaline; it is the only heavy metal which forms a soluble oxide, hydroxide and carbonate.

The Thallic compounds resemble the compounds of Aluminum.

Group IV.

The elements of this group have the oxide formula E_2O_4 or EO_2, showing a valence of 2. Like the other groups, it is subdivided into two families.

Family A—the elements belonging to the even series of the long periods. These are: Titanium, Zirconium, Cerium and Thorium. All but Cerium have been mentioned in the non-metals. The natural compounds of Thorium show radio activity. Thorium is used in the Welsbach mantle. Zirconium-oxide, ZrO_2, is used in the so-called Zirconium light, which is an Oxy-Hydrogen flame, containing a piece of Zirconium-oxide.

CERIUM.

SYMBOL, Ce,; AT. MASS, 139.2; VAL. 3, 4.

This is contained along with other rare metals (Lanthanum, Didymium, Ytterbium, Erbium, etc.) in the minerals *cerite, gadolite,* etc. It is official as Cerium-oxalate, a white powder without taste or odor, insoluble in water, used as an anti-emetic. It is really a mixture of the oxalates of Cerium, Lanthanum, Didymium and other rare metals.

Family B—those elements belonging to the short periods, and to the odd series of the long periods, of the fourth group. They are Carbon, Silicon, Germanium, Tin and Lead. Carbon and Silicon have been studied. Germanium, Tin and Lead have a valence of 2 and 4, Lead being more commonly 2.

LEAD (Plumbum).

SYMBOL, Pb; AT. MASS, 205.35; VALENCE, II.

Lead is a heavy, easily-fusible metal, and at high temperature can be vaporised. It is insoluble in sulphuric and hydrochloric

acids, but soluble in nitric and acetic acids. When highly heated in air, its surface becomes oxidised, a coating of Lead-oxide forming a scum over the liquid. This can be removed layer after layer until all the metal is converted into Lead-oxide.

Lead is soft and ductible, and leaves gray lines on paper. It is somewhat soluble in pure water if in contact with air, as it forms slightly-soluble Lead-hydroxide; but is insoluble in water containing Carbon-dioxide. It is therefore safe to use it for water-pipes, as drinking water contains Carbon-dioxide.

Lead is found native as *galena* (Lead-sulphide). This is converted into metallic Lead in various ways; for instance, by heating it with metallic Iron:

The Lead salts are mostly colorless or white; except the oxides, which are yellow, red or brown, the iodide, which is yellow, and the sulphide, which is black.

In its principal compounds, Lead has a valence of 2. They are called the Plumbic compounds, or Lead salts.

The 4-valent Lead is rare, and occurs in a few compounds of little importance like

Lead-tetrachloride ($PbCl_4$)— a yellow, oily liquid, fuming in air, and easily decomposed into $PbCl_2$ and Chlorine.

Lead-dioxide—see later.

OXIDES OF LEAD.

The principal oxides of Lead are

Lead-oxide (Plumbi oxidum), PbO

This is also called *litharge,* and is a heavy powder, insoluble in water, but soluble in dilute nitric and acetic acids. It is prepared by heating metallic Lead in air. It has alkaline properties, but will dissolve in Potassium-hydroxide.

Dioxide of Lead, or Lead-peroxide (PbO_2)

A dark-brown powder, insoluble in water and in dilute nitric and acetic acids. It is a strong oxidising agent; and if boiled with hydrochloric acid, frees Chlorine:

$$PbO_2 + 4HCl = 2H_2O + PbCl_2 + 2Cl$$

It dissolves in Potassium-hydroxide, forming Potassium-plumbate, K_2PbO_3; plumbic acid being $PbO_2 + H_2O = H_2PbO_3$.

Red Lead (Minium)

A compound of two molecules of litharge with one molecule of Lead-dioxide: $2PbO + PbO_2 = Pb_3O_4$. A red, heavy powder, insoluble in water. If treated with nitric acid, the litharge part dissolves, but not the dioxide part. If treated with hydrochloric acid, the dioxide portion causes an evolution of Chlorine. It is prepared by heating litharge in air, which takes up Oxygen and is converted into red Lead. It is a strong oxidising agent.

Lead-nitrate (Plumbi nitras), $Pb(NO_3)_2$

White crystals, soluble in water. Prepared by dissolving litharge in nitric acid.

Lead-chloride (Plumbi chloridum), $PbCl_2$

White crystals, almost insoluble in cold water, more soluble in hot water; when its hot solution is cooled, it precipitates in long needles. Prepared by precipitating a solution of Lead-nitrate with a solution of Sodium-chloride.

Lead-iodide (Plumbi iodidum), PbI_2

A bright-yellow powder, almost insoluble in cold water, rather more soluble in hot. Prepared by precipitating a solution of Lead-nitrate with one of Potassium-iodide.

Lead-acetate (Plumbi acetas), $Pb(CH_3COO)_2$

Also known as *sugar of Lead.* White, efflorescent crystals of sweet taste, soluble in water. Distilled water must be used, as the sulphates of ordinary water form precipitates. Lead-acetate has a faint odor of acetic acid, and gradually loses some acetic acid and forms Lead-acetate. It is prepared by dissolving Lead-oxide in acetic acid.

Lead-subacetate (Plumbi subacetas)

This is Lead-acetate plus Lead-oxide, and is official in a 25 percent solution as *Goulard's extract* (*liquor Plumbi sub-ace-*

tatis). This is prepared by heating sugar of Lead with water and Lead-oxide, and filtering. If Carbon-dioxide is passed through its solution, this combines with the oxide and forms insoluble Lead-carbonate, while Lead-acetate remains in solution. The carbonate encrusts the walls and bottom of the vessel.

Lead-carbonate (Plumbi carbonas), $PbCO_3$

Also called *white Lead.* A heavy, white powder, insoluble in water but soluble in acids, where it effervesces. It is in reality a subcarbonate of Lead, and has a formula of $2PbCO_3 + Pb(OH)_2$. Used much for paints.

It is prepared in many different ways, the principal of which are:

1. *The Dutch process.* Lead-plates are rolled and placed in jars having double bottoms, the lower compartments of which contain acetic acid. These jars are loosely covered, and put into manure and there left for some considerable time. The heat of the manure evaporates the acetic acid, and the vapors act on the Lead-plates and form Lead-subacetate; this, with the CO_2 of the manure, forms Lead-carbonate. This process yields the finest white Lead.

2. *French process.* Lead-oxide in excess is treated with vinegar, and Lead-subacetate is formed. The solution is allowed to settle, and the clear liquid drawn off into a second vessel. Carbon-dioxide is then passed into this, and the Lead-subacetate is changed into Lead-carbonate (which settles out) and Lead-acetate in solution. The Lead-acetate is then put back into the first vessel and treated with Lead-oxide, and so the process reiterates.

Tests for Lead. 1, Hydrogen-sulphide gives a black precipitate in any solution. 2, Sulphuric acid gives a white precipitate of Lead-sulphate. 3, Hydrochloric acid gives a white precipitate of Lead-chloride, soluble in large amounts of boiling water, but again crystallising on cooling. 4, Potassium-chromate gives a yellow precipitate.

TIN (Stannum).

SYMBOL, Sn; AT. MASS, 118; VALENCE, II, IV.

Tin is a Silver-white metal, fusing at low temperature. It is not readily oxidised in air; can be beaten out into thin sheets; and is somewhat crystalline. If a bar of Tin is bent, it emits a faint sound, the 'tin cry'; this is caused by its crystalline nature. It is found in many alloys—bronze, solder, Britannia metal, etc.

When Tin is treated with hydrochloric acid, the metal is dissolved and Hydrogen freed. Not so with nitric acid, which converts it into a white, amorphous powder (meta-stannic acid) and evolves Nitrogen-dioxide gas.

Tin occurs native as *Tinstone* (*Tin-oxide*). The pure metal is obtained by reducing this with Carbon.

The principal Tin compounds are the two chlorides:

Stannous-chloride ($SnCl_2$)

Commonly called Tin-salt, is a white, soluble salt. If dissolved in a large quantity of water, it forms the white, insoluble oxy-chloride. Stannous-chloride is a strong reducing agent, readily taking up Chlorine or Oxygen. If brought together with Mercuric-chloride, it robs this latter of Chlorine and Mercurous-chloride or metallic Mercury result:

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg$$

Stannous-chloride is prepared by dissolving Tin in hydrochloric acid, and evaporating the solution obtained.

Stannic-chloride ($SnCl_4$)

Can be prepared by oxidising Stannous-chloride, or by passing Chlorine through a solution of the latter. It is used as a mordant under the name *proto-chloride* or *oxy-muriate* of Tin. It is a colorless, mobile, volatile liquid, which fumes in air.

OXIDES OF TIN.

Stannous-oxide (SnO)

A white powder, insoluble in water but soluble in Sodium-

hydroxide, forming Sodium-stannite (Na_2SnO_2), a salt used in calico-printing.

Stannic-oxide (SnO_2)

Occurs as Tinstone, the most important ore of Tin. A white solid or powder, changing to yellow on the application of heat. This yellow color disappears, however, on cooling. Fused with Sodium-hydroxide, it forms Sodium-stannate, Na_2SnO_3, used as a mordant.

SULPHIDES OF TIN.

Stannous-sulphide (SnS)

A brown powder, insoluble in water. Prepared by passing Hydrogen-sulphide through an acid solution of Stannous-chloride.

Stannic-sulphide (SnS_2)

A yellow substance, insoluble in water. Prepared by passing Hydrogen-sulphide through an acid solution of a Stannic salt. Used in bronzing under the name *mosaic Gold.*

The sulphides of Tin are sulpho-acids, and unite with sulpho-bases to form soluble sulpho-salts.

GERMANIUM.

SYMBOL, Ge; AT. MASS, 71.9; VALENCE, II, IV.

Predicted by Mendeljeff, and discovered by Winkler. Forms Germanous and Germanic compounds. Not important.

Group V.

The elements of this group are characterised by the oxide-formula E_2O_5, showing a valence of 5.

Family A—the elements of the even series of the long periods. They are: Vanadium, Columbium (Niobium), Tantalum.

They have been mentioned before.

Family B—those elements of the short periods, and of the odd series of the long periods. They are: Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth. All have been studied except Bismuth.

BISMUTH.

SYMBOL, Bi; AT. MASS, 206.9; VALENCE, III (V).

A gray metal, of a reddish tint, crystalline in structure. Can be fused with ease, some of its alloys even melting in hot water. It is much employed in alloys. Bismuth does not readily change when exposed to air, but, if heated sufficiently, burns and forms the oxide, Bi_2O_3. It is soluble in nitric acid.

Most of its salts are colorless or white; the oxide Bi_2O_3 is yellow, the sulphide Bi_2S_3 is black, and the iodide and bromide are colored.

When concentrated solutions of Bismuth salts are mixed with water, they become milky and form a white preciptate of a basic salt or *Bismuthyl salt.*

There are, then, the regular Bismuth salts regularly built from trivalent Bismuth, as $Bi(NO_3)_3$; and Bismuthyl salts, formed from the univalent radicle —Bi=O, in which two valences of the trivalent Bismuth are satisfied by a bivalent Oxygen atom. The radicle (BiO) behaves as one element:

$(BiO)NO_3$, Bismuthyl-nitrate.

$(BiO)_2SO_4$, Bismuthyl-sulphate.

$(BiO)_2CO_3$, Bismuthyl-carbonate.

These Bismuthyl salts are also called *basic Bismuth salts, subsalts of Bismuth, Bismuth oxy-salts.* They are insoluble in water, but soluble in acids, forming the regular Bismuth salts.

$$(BiO)NO_3 + 2HNO_3 = Bi(NO_3)_3 + H_2O$$

They are usually white powders, and are prepared by the addition of water to the regular Bismuth salts—these break down into the Bismuthyl salt and free acid. The acid is too dilute to dissolve the Bismuthyl salt, which precipitates and gives a milky appearance to the solution. (test for Bismuth). Native Bismuth occurs in rocks, and is obtained by crushing and heating these. It is also found as the sulphide and as the oxide.

Bismuth-nitrate, $Bi(NO_3)_3$

Colorless crystals, soluble in water containing nitric acid. If much water is present, the Bismuthyl-nitrate precipitates.

Prepared by dissolving metallic Bismuth in nitric acid.

Bismuthyl-nitrate (Bismuthi subnitras), $BiO.NO_3 + H_2O$

Also called *Bismuth-oxy-nitrate* or *magisterium Bismuthi,* a white, powder, insoluble in water but soluble in acids. Heat changes it into the yellow Bismuth-oxide (Bi_2O_3).

Prepared by treating Bismuth-nitrate with an excess of water.

Bismuth-subcarbonate (Bismuthi subcarbonas), $(BiO)_2CO_3 + 2\ H_2O$

Also called *Bismuthyl-carbonate* and *Bismuth-oxycarbonate,* a white powder, insoluble in water but soluble with effervescence in acids. Prepared by heating a solution of Bismuth-nitrate with Sodium-carbonate.

Bismuth-oxide (Bismuthi oxidum), Bi_2O_3

Yellow powder, insoluble in water but soluble in acids.

Prepared by burning metallic Bismuth in air, or by heating Bismuthyl-carbonate or Bismuthyl-nitrate or hydroxide.

Bismuthyl-hydroxide, BiO.OH

Also called *Bismuth-oxyhydrate,* a white powder, insoluble in water but soluble in acids, forming the regular Bismuth salt. Prepared by treating a solution of a Bismuth salt with one of Ammonium-, Potassium- or Sodium- hydroxide.

The regular Bismuth-hydroxide, $Bi(OH)_3$, is sometimes formed when an acid solution of Bismuth-nitrate is poured into an excess of strong ammonia-water. This is also a white powder, insoluble in water but soluble in acids.

Bismuth-trichloride, $BiCl_3$

A white, deliquescent, crystalline mass. With much water, it decomposes and forms Bismuthyl-chloride (BiO.Cl) and hydrochloric acid:

$$BiCl_3 + H_2O = BiO.Cl + 2HCl$$

It may be prepared by passing dry Chlorine over heated metallic Bismuth.

Bismuthyl-chloride, BiO.Cl

White powder insoluble in water but soluble in concentrated acids. Prepared by decomposing Bismuth-trichloride with water.

Tests for Bismuth. 1, With much water, Bismuth solutions form a precipitate of a Bismuthyl salt. 2, Hydrogen-sulphide gives a dark-brown precipitate. 3, Ammonium- or Potassium-hydroxide give a white precipitate of Bismuthyl-hydroxide.

Group VI.

This group consists of elements with the general oxide-formula E_2O_6 or EO_3, showing a maximum valence of 6.

Family A—the elements of the even series of the long periods. They are: Chromium, Molybdenum, Tungsten and Uranium.

Family B—consisting of Oxygen, Sulphur, Selenium and Tellurium. These have been treated of with the non-metals.

CHROMIUM.

SYMBOL, Cr; AT. MASS, 51.7; VALENCE, III, VI.

Chromium is sometimes bivalent. Such compounds are, however, of no importance.

Chromium is a hard, gray metal, difficult to fuse and not changed by exposure to air. Fused with steel, it increases the hardness of the latter very much. It is found in nature in combination with Iron and Oxygen as *Chrome Iron ore* or *chromite,* an ore insoluble in all known solvents. The Chromium contained is rendered soluble by fusing the ore with lime and Potassium-carbonate in an oxidation-furnace; Potassium-chromate and Ferric-oxide are formed. The Potassium-chromate is dissolved out with water, crystallised, and used for the preparation of other Chromium compounds.

The compounds of Chromium are usually vividly colored, hence the name of the element—derived from the greek for color.

There are two principal classes of Chromium compounds:

1. Those in which Chromium is trivalent. Here Chromium acts as a base and unites with acids to form Chromic salts, which are green or violet in color.

2. Those compounds in which Chromium is 6-valent. Here Chromium acts as an acid (chromic acid) and its salts, the chromates, are yellow or red.

OXYGEN COMPOUNDS OF CHROMIUM.

Chromium-trioxide (Chromii trioxidum), CrO_3

Often called *chromic acid,* although not a real acid, being minus the necessary water. Occurs as scarlet, needle-shaped crystals, very deliquescent, and soluble in water. It is a strong oxidising agent, giving up Oxygen and changing into the green sesquioxide of Chromium:

$$2CrO_3 = Cr_2O_3 + 3O$$

It should not be mixed with burnable substances, as it oxidises them so rapidly as to cause serious explosions. If boiled with sulphuric acid, it evolves Oxygen:

$$2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + 3O$$

Boiled with hydrochloric acid, it evolves Chlorine:

$$CrO_3 + 6HCl = CrCl_3 + 3H_2O + 3Cl$$

It is employed in medicine as a caustic, as it oxidises the tissues. It is prepared by treating a concentrated solution of Potassium-chromate with strong sulphuric acid. The crystals which this reaction produces are filtered from the solution by means of glass-wool, and dried in a current of air.

With water, it forms two acids:

$$CrO_3 + H_2O = H_2CrO_4, \text{ chromic acid.}$$
$$2CrO_3 + H_2O = H_2Cr_2O_7, \text{ dichromic acid.}$$

The salts of chromic acid are called *chromates* and are of a yellow color. The salts of dichromic acid, the *dichromates,* are red. Both classes of salts are strong oxidising agents, and should not be mixed with combustible material.

If boiled with sulphuric acid, green Chromium-sulphate $Cr_2(SO_4)_3$, the sulphate of the metal and free Oxygen result:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

Boiled with hydrochloric acid, green Chromium-chloride, the chloride of the metal present in the original compound, and free Chlorine are formed.

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O$$

Potassium-chromate (Potassii chromas), K_2CrO_4

Yellow chromate of Potassium. Yellow crystals, soluble in water. Prepared by melting Chrome-Iron ore with Calcium and Potassium-carbonate; or by the addition of Potassium-hydroxide to Potassium-dichromate.

Potassium-dichromate (Potassii dichromas), $K_2Cr_2O_7$

Red chromate of Potassium. Red crystals, soluble in water. Prepared by treating yellow Potassium-chromate with a little sulphuric acid, and separating the Potassium-dichromate out by crystallisation.

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O$$

Treated with hydroxides or carbonates of the alkali-metals, the dichromate changes into the yellow chromate:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$$

Lead-chromate (Plumbi chromas), $PbCrO_4$

A yellow powder, insoluble in water, used in paints as *chrome yellow.* Prepared by precipitating a Lead solution with one of Potassium- chromate or dichromate.

When a solution of a chromate or a dichromate is boiled with sulphuric or hydrochloric acid, the color of the salt changes to green and Oxygen or Chlorine is evolved. In these green salts Chromium is tri-valent. If treated with ammonia-water, a green precipitate of Chromium-hydroxide is thrown down which is soluble in dilute acids and in cold (but not in hot) Potassium-hydroxide.

The different Chromium salts can be prepared by dissolving Chromium-hydrate in the necessary acid; as Chromium-chloride by dissolving Chromium-hydroxide in hydrochloric acid.

Chromic-oxide (Chromium sesqui-oxide), Cr_2O_3

A green powder, insoluble in water, and, if much heated, in acids also. It is commonly known as *chrome green,* and is employed in paints. It is prepared by heating Chromic-hydroxide, $2Cr(OH)_3 = Cr_2O_3 + 3H_2O$. Also by heating a mixture of Potassium-dichromate and Sulphur. The Sulphur is oxidised

to sulphuric acid, and this unites with the Potassium and forms Potasssium-sulphate; the Chromic acid is reduced to Chromic-oxide.

Chrome alum, $CrK(SO_4)_2 + 12H_2O$

Violet crystals, soluble in water. Prepared by treating Potassium-chromate with sulphuric acid and passing Sulphur-dioxide through it; this reduces the solution, forming Chromic-sulphate and Potassium-sulphate. The solution is then crystallised.

Tests for Chromium in the trivalent condition: Ammonia-water gives a green precipitate of Chromium-hydroxide, soluble in a cold solution of Potassium-hydroxide—forms again on heating.

For 6-valent compounds. 1, Boiling with hydrochloric acid and alcohol changes to green salts,which give tests for trivalent Chromium. 2, The addition of Sodium-acetate to an acid solution, or of acetic acid to an alkaline one, and then Lead-acetate gives a precipitate of chrome yellow.

General test for all Chromium compounds: Melt the substance to be tested together with Potassium-carbonate and Potassium-nitrate; dissolve the mass in water; filter. The filtrate will be yellow if Chromium is present.

MOLYBDENUM.

SYMBOL, Mo; AT. MASS, 95.3; VALENCE, II, IV, VI.

This is a comparatively rare element. It is hard, and has a high melting point. The most important of its compounds is *Molybdenum-trioxide,* MoO_3. This is obtained by burning the metal in air. It is a white mass, insoluble in water and acids, soluble in alkalies to form salts, the *molybdenates.* In these salts we assume the presence of *molybdenic acid,* H_2MoO_4.

Ammonium-molybdenate $(NH_4)_2MoO_4$, is a white salt, soluble in water, used as a test for phosphoric acid, with which it gives a yellow precipitate in nitric acid solution. Hereby complex acids, the *phospho-molybdenic acids,* are formed. These form

salts with Potassium, Ammonium, Thallium and the alkaloids which are insoluble in dilute acids but soluble in alkalies.

In the test for phosphoric acid, Ammonium-phospho-molybdenate, $(NH_4)_3PO_4,11MO_3$, is formed; and, being insoluble in nitric acid, precipitates as a yellow, crystalline powder.

Phospho-molybdenic acid is also used as a test for alkaloids.

Arsenic acid produces similar compounds with Molybdenum-trioxide.

TUNGSTEN (Wolframium).

SYMBOL, W; AT. MASS. 182.6; VALENCE, II, IV, VI.

Tungsten resembles Molydbenum. It forms an acid, *tungstic acid,* H_2WO_4, the Sodium salt of which is used as a mordant and for fireproofing clothes, etc. It forms poly-acids:

$$2WO_3 + H_2O = H_2W_2O_7, \text{ di-tungstic acid.}$$
$$4WO_3 + H_2O = H_2W_4O_{13}, \text{ tetra-tungstic acid.}$$

The latter is also called meta-tungstic acid. It forms the complex phospho-tungstic acids, used as a test for alkaloids, albumin, etc.

URANIUM.

SYMBOL, U; AT. MASS, 236.7; VALENCE, IV, VI.

This metal occurs principally in pitchblende. It possesses radio activity, as do its compounds. It forms Uranous compounds, in which the metal is 4-valent, and Uranic compounds, in which it is 6-valent. The only important salts are the *Uranyl salts,* formed from the bivalent radicle ($=UO_2$). Uranyl-nitrate, $UO_2.(NO_3)_2$, occurs as greenish-yellow crystals, soluble in water. It is employed in the volumetric test for phosphoric acid, with which it gives a yellow precipitate. Potassium-ferrocyanide gives a brown precipitate with Uranyl-salts. Uranyl-acetate is also used as a test for phosphoric acid.

Group VII.

This group is characterised by the oxide-formula E_2O_7, showing a maximum valence of 7. All the elements of the group are non-metals except Manganese, which belongs to family A.

MANGANESE.

SYMBOL, Mn; AT. MASS, 54.6; VALENCE, II, III, VI, VII.

This metal resembles metallic Iron. It is found as Manganese-dioxide (MnO_2), a black ore. Manganese forms four classes of compounds:

1. *Manganous salts.* Here the Manganese is bivalent and the color of the compounds is a light pink. In diluted solutions, this color cannot be distinguished. These are the most stable of the Manganese compounds (except the oxide and hydroxide). Other salts, in which Manganese has a valence of more than 2, easily split up into Manganous salts and Oxygen—or Chlorine, if hydrochloric acid is present.

2. *Manganic salts.* In these Manganese is trivalent. They are of a brown color, and stable only in chilled condition. If heated, they give up Oxygen or Chlorine and change into the Manganous salt:

$$MnCl_3 = MnCl_2 + Cl$$

They are not important.

3. *Manganic acid and its compounds.* Manganese here shows a valence of 6. They are dark-green in color, and are not stable; readily giving up Oxygen and changing into Manganous salts.

$$K_2MnO_4 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + 2O$$

4. *Permanganic acid and permanganates.* The valence of Manganese in them is 7. They are dark-violet in color, and not stable. They readily give up Oxygen and change into the Manganous compounds:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

OXIDES OF MANGANESE.

MnO, Manganous-oxide.
Mn_3O_4, Manganous-Manganic-oxide ($MnO + Mn_2O_3$)
Mn_2O_3, Manganic-oxide.
MnO_2, Manganese-dioxide.
MnO_3, Manganese-trioxide.
Mn_2O_7, Manganese-heptoxide.

Of these six oxides of Manganese, the Manganous-Manganic is the most stable at high temperature. All the higher oxides evolve Oxygen if heated, and form the Manganous-Manganic-oxide:

$$3MnO_2 = Mn_3O_4 + 2O$$

The lower oxide MnO takes up Oxygen when heated in air, and forms Manganous-Manganic-oxide:

$$3MnO + O = Mn_3O_4$$

On boiling with sulphuric acid, all but Manganous-oxide evolve Oxygen:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$

If treated with hydrochloric acid, all except Manganous-oxide evolve Chlorine.

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + 2Cl$$

Manganese-dioxide (Mangani dioxidum), MnO_2

Also called black oxide of Manganese, is found in nature as a black ore, insoluble in water. If heated, it evolves Oxygen; leaving Manganous-Manganic-oxide, Mn_3O_4. Boiled with sulphuric acid, it forms Manganous-sulphate and Oxygen. Boiled with hydrochloric acid, Manganous-chloride and free Chlorine

result. The official form should contain at least 80 percent MnO_2. It is prepared by mixing a solution of Manganous-sulphate with a mixture of ammonia and Hydrogen-dioxide. The latter oxidises the precipitated Manganous-hydroxide.

Manganous-sulphate (*Mangani sulphas*), $MnSO_4$

Pink crystals, containing water of crystallisation; soluble in water. Prepared by boiling black oxide of Manganese with sulphuric acid—Oxygen being set free.

Manganous-hypophosphite (*Mangani hypophosphis*), $Mn(PO_2H_2)_2$

A pink, crystalline powder, odorless and almost tasteless. Soluble in water. Prepared by precipitating a solution of Barium-hypophosphite with one of Manganous-sulphate. The filtrate is evaporated.

Manganous-chloride (*Mangani chloridum*), $MnCl_2$

Pinkish crystals, soluble in water. Prepared by boiling Manganese-dioxide with hydrochloric acid—Chlorine is evolved.

Manganic acid, H_2MnO_4

Not known in the free state. Its salts, the *manganates,* are dark-green in color, and are not stable, readily giving up their Oxygen, and forming Manganous compounds. They are therefore excellent oxidising agents. If treated with hydrochloric acid, they evolve Chlorine.

If a solution of a manganate is much diluted with water, heated, or Carbon-dioxide passed through it, it decomposes. Manganese-dioxide is precipitated, while the violet permanganate formed remains in solution:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$$

The color changes from green to violet.

Prepared by melting together Manganese-dioxide, Potassium-chlorate and Potassium-hydroxide:

$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O$$

Permanganic acid, $Mn_2O_7 + H_2O = H_2Mn_2O_8$ *or* $HMnO_4$

This acid is not important, but its salts are. They are the *permanganates,* and are violet-colored. They are strong oxidising agents.

Potassium-permanganate (Potassii permanganas), $KMnO_4$

Small, blackish crystals, of metallic lustre, soluble in water. Its solution has a violet color, and is a very strong oxidising agent. Boiled with hydrochloric acid, it evolves Chlorine and forms Potassium- and Manganous- chlorides, the violet solution becoming colorless

$$KMnO_4 + 8HCl = KCl + MnCl_2 + 4H_2O + 5Cl.$$

If treated with a substance capable of taking up Oxygen, in the presence of sulphuric acid, it forms Potassium-sulphate and Manganous-sulphate. This solution is also colorless.

Thus reducing agents will decolorise a solution of Potassium-permanganate.It is used in analytical chemistry in testing for sulphurous acid, sulphites, hypophosphites, Ferrous salts and other reducing agents.

It is prepared by melting together Manganese-dioxide and Potassium-chlorate and Potassium-hydroxide, boiling the mass with water, and passing Carbon-dioxide through the solution. This is filtered through wool-glass, and evaporated to crystallisation.

Tests for Manganese. 1, With Hydrogen-sulphide in alkaline solution, it forms a flesh-colored precipitate of Manganese-sulphide, soluble in dilute acids. 2, Sodium-, Potassium-, and Ammonium- hydroxides each give a white precipitate, which darkens by the absorption of Oxygen. 3, When a Manganese compound is melted with saltpeter and Sodium-carbonate, it yields a dark-green mass; when this is boiled with water and a little sulphuric acid, a violet color results.

Group VIII.

The elements of this group connect the seventh member of the even series of the long period with the first of the odd series. They are therefore known as *transitional elements.*

The valence of 8 and the oxide-formula of E_2O_8 (EO_4) is only attained in a few instances (Osmium, etc.); the important compounds of these elements are built up from lower valences.

The group consists of nine elements, which may be subdivided into three families:

Family A—those of the first long period. Iron, Nickel and Cobalt.

Family B—those of the second long period: Ruthenium, Rhodium and Palladium.

Family C—those of the fourth long period: Osmium, Iridium and Platinum.

Family A—the Iron Family.

The main valence of these elements, Iron, Nickel and Cobalt, is 2 and 3—Nickel and Cobalt being more commonly 2. Iron in a few instances shows a valence of 6, as in Iron-trioxide (FeO_3). This compound is acid in nature, and unites with Potassium-hydroxide to form Potassium-ferrate, K_2FeO_4. Here we assume the presence of ferric acid, H_2FeO_4, which is analagous to sulphuric, chromic and manganic acids. The compounds of the bivalent Iron, Nickel and Cobalt resemble the corresponding compounds of Zinc and Copper, while the trivalent compounds resemble those of Aluminum.

The elements of this family are further distinguished by the ease with which they become magnetised, and by their ability to form complex compounds with the cyanogen radicle.

IRON (Ferrum).

SYMBOL, Fe; AT. MASS, 55.5; VALENCE, II, III.

Iron is a gray metal, having a specific gravity of 7.84. It is difficult to fuse. It is attracted by the magnet, and can become itself a magnet. Dilute acids dissolve it, Hydrogen being evolved and a green Ferrous salt formed. In moist air it *rusts;* that is, forms an oxide.

Iron is almost universally distributed throughout nature, in plants and animals as well as in minerals. The most important of its ores are *hematite,* (Iron-oxide), Iron-carbonate and Iron-sulphide.

Iron is usually prepared by roasting the oxide with coal in large 'blast furnaces.'

$$Fe_2O_3 + 3C = Fe_2 + 3CO$$

Technically, three different forms of Iron are recognised:

Cast Iron or *Pig Iron,* containing about 4 percent of Carbon, which affects the properties of the metal. It is easily fused and can be cast, but is hard and brittle. It cannot be used for the manufacture of articles which are needed to resist great and sudden strain, as it breaks readily.

Wrought Iron is nearly chemically pure, and contains little Carbon. It is very hard to melt, but at red heat becomes soft and can be kneaded—a process called *forging* or *welding.* It bends when subjected to sudden stress.

Steel. This form contains some Carbon (about 1.5 percent). and its properties, like the amount of Carbon present, are roughly the mean of the other two forms. It can be forged as well as cast, is hard as cast Iron and resistant as wrought Iron. When steel is heated in a nonluminous flame, it becomes blue, yellow, reddish, etc. according to the length of time it is exposed to heat.

Manufacture of Cast Iron: By heating Iron ores with coal in blast furnaces.

Manufacture of Wrought Iron.

By puddling—melting cast Iron, and stirring the mass continually in the presence of air until it becomes thick in

consistency. By this means the Carbon is oxidised.

Manufacture of Steel.

By cementation — heating wrought Iron with the proper amount of coal.

By the Bessemer process — oxidising the Carbon in pig-iron by blowing air through the molten mass. The Carbon can also be oxidised by puddling.

Metallic Iron is official in two forms: Iron wire (*Ferrum*) and reduced Iron (*Ferrum Hydrogenio reductum*), also called 'Quevenne's Iron.' The latter is a fine, grayish-black powder, prepared by heating Iron-oxide and passing Hydrogen over it. The Hydrogen takes the Oxygen from the Iron and forms water, leaving the metal reduced.

Iron preparations are used in medicine as astringents and haemostatics, and as tonics in anemia.

Iron forms two classes of compounds:

Ferrous compounds, green in color, in which Iron is bivalent. They are easily prepared by dissolving the metal in acids. If exposed to air or oxidising agents, they form the Ferric salts.

Ferric compounds, which are brown. Here Iron is trivalent. They are prepared by oxidising the Ferrous salts, usually with nitric acid.

FERROUS COMPOUNDS.

Ferrous-sulphate (*Ferri sulphas*), $FeSO_4$

Green crystals, soluble in water but insoluble in alcohol. It is commonly called *copperas or green vitrol.* It contains 7 molecules of water of crystallisation, is somewhat effiorescent, and when exposed to air becomes gradually oxidised to brown, basic Ferric-sulphate.

Ferrous-sulphate is prepared by dissolving metallic Iron in sulphuric acid, Hydrogen being evolved. It is official in three forms: 1, In crystals (*Ferri sulphas*). 2, In granulated form, (*Ferri sulphas granulatus*), prepared by treating a hot satur-

ated aqueous solution of the crystals with a little sulphuric acid, and cooling the solution quickly under constant agitation. 3, In exsiccated form (*Ferri sulphas exsiccatus*), prepared by reducing Iron-sulphate to a coarse powder, allowing it to effloresce and then heating on a waterbath to drive out all water of crystallisation. A white powder remains.

Ferrous-iodide (*Ferri iodidum*), FeI_2

A green salt, readily soluble in water and easily oxidised to a basic Ferric salt (brown), liberating Iodine by conversion. It is prepared by treating an excess of Iron wire with water and Iodine. This is filtered and sugar added as a reducing agent to keep the solution green. It is official in two forms:

Syrup of Ferrous-iodide: A green syrup containing 5 per-cent of Ferrous-iodide. It is prepared by treating an excess of Iron wire with water and Iodine, adding the Iodine gradually, allowing the color to become green before each increment. It is then filtered, and sugar added. The U. S. P. uses hypophosphorous acid as a reducing agent to keep the syrup green.

Pills of Ferrous-iodide (*Pilulae Ferri iodidi*), also known as 'Blanchard's' pills.

Ferrous-carbonate (*Ferri carbonas*), $FeCO_3$

A light-green powder, insoluble in water but soluble in acids, where it effervesces. It is very easily decomposed, taking up Oxygen and forming brown Ferric-oxide, Carbon-dioxide escaping. In order to prevent this, The U. S. P. advises mixing with sugar. It is official in four forms:

1. *Saccharated Ferrous-carbonate* (*Ferri carbonas saccharatus*). This is prepared by mixing a solution of Sodium-bicarbonate and one of Ferrous-sulphate. A precipitate of Ferrous-carbonate is formed, and this is washed with water. The precipitate is mixed with sugar and evaporated to dryness.

2, *Vallet's Mass* (*massa Ferri carbonatis*). Prepared by adding a little syrup to a solution of Ferrous-sulphate, and mixing this with one of Sodium-carbonate. The precipitate formed is washed with water containing syrup (to prevent oxidation)

and then sugar and honey are added. The mixture is finally evaporated to the weight of the Iron-sulphate employed.

3. *Pills of carbonate of Iron* (*pilulae Ferri carbonatis*), known as 'Blaud's pills' See U. S. P.

4. *Griffith's mixture* (*mistura Ferri composita*). See U.S.P.

Ferrous-hydroxide (*Ferri hydroxidum*), $Fe(OH)_2$

Prepared by adding a solution of Potassium-hydroxide to one of a Ferrous salt. It is obtained as a light-green precipitate, readily oxidised, becoming then darker in color and finally brown—indicating its conversion into the Ferric-hydroxide.

FERRIC COMPOUNDS.

Ferric sulphate (*Ferri sulphas*), $Fe_2(SO_4)_3$

This is official in three forms:

1. *Liquor Ferri tersulphatis,* a brown liquid containing 10 percent of metallic Iron.

2. *Liquor Ferri subsulphatis* (*Monsel's solution*), a brown, heavy liquid containing 13.5 percent of metallic Iron

The two above solutions can be differentiated by mixing them with strong sulphuric acid. Monsel's solution forms a white, sticky precipitate; the tersulphate remains clear.

Both are prepared by mixing nitric and sulphuric acids together and heating, powdered Ferrous-sulphate being added at intervals. The solution obtained is then evaporated to drive out the excess of nitric acid, and diluted to the correct percentage.

3. *Iron and Ammonium-sulphate* (*Ferri et Ammonii sulphas*), $FeNH_4(SO_4)_2,12aq,$ is a double salt of Ammonium-sulphate and Ferric-sulphate, and contains 12 molecules of water of crystallisation. It is also called *Iron-Ammonium-alum* and occurs as light-violet crystals, soluble in water. It is prepared by mixing solutions of Iron-tersulphate and Ammonium-sulphate together, and crystallising.

Ferric-chloride (Ferri chloridum), $FeCl_3$

This is official in two forms; *crystalline*—a brown, deliquescent mass, soluble in water. Prepared by evaporating the aqueous solution to dryness; and as *liquor Ferri chloridi,* a brown liquid containing 10 percent of metallic Iron. Prepared by dissolving metallic Iron in hydrochloric acid, Ferrous-chloride and free Hydrogen being formed. The solution is then filtered. It is green in color. Nitric and hydrochloric acids are now added and the mixture boiled, the Ferrous-chloride being oxidised to Ferric-chloride, a brown solution. The excess of nitric acid is driven off by evaporation.

Ferric-hydroxide (Ferri hydroxidum), $Fe(OH)_3$

A brown, voluminous substance, insoluble in water but soluble in acids. If kept for a long time or if heated, it decomposes and forms a complex compound of the formula $2Fe(OH)_3$—1 or 2 molecules of water. These compounds are not as readily soluble in acids, especially acetic acid. In the moist state, freshly prepared, Ferric-hydroxide unites with Arsenic and forms an insoluble compound. It is therefore used as an antidote against Arsenic poisoning. Only the freshly prepared hydroxide has this property, not the compounds formed by decomposition.. It is prepared by adding any soluble hydroxide to a solution of a Ferric salt.

It is official in two forms, both in moist state, and both used as antidotes for Arsenic poisoning.

1. *Ferri hydroxidum.* Obtained by precipitating a solution of tersulphate of Iron with ammonia-water, collecting the precipitate in a muslin strainer, washing and drying. It is dispensed moist.

2. *Ferri hydroxidum cum Magnesii oxido.* Prepared by triturating calcined Magnesia with water, forming Magnesium-hydroxide. This is mixed with a solution of tersulphate of Iron, and Iron-hydroxide (the antidote) precipitates, Magnesium-sulphate remaining in solution and acting as a laxative.

Ferric-carbonate, $Fe_2(CO_3)_3$

It cannot be prepared artificially, decomposing at once into Carbon-dioxide and Ferric-oxide:

$$Fe_2(CO_3)_3 = Fe_2O_3 + 3CO_2$$

If a solution of a soluble carbonate is mixed with a solution of a Ferric salt, a brown precipitate of Ferric-hydroxide results and Carbon-dioxide escapes:

$$Fe_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Fe(OH)_3 + 3Na_2SO_4 + 3CO_2$$

Other trivalent elements, as Aluminum, Chromium, Manganese, behave in similar fashion.

Ferric-phosphate (Ferri phosphas), $FePO_4$

Insoluble in pure water, soluble in water containing Sodium-citrate. The official phosphate of Iron, called soluble Iron-phosphate, is made soluble by the presence of Sodium-citrate. Prepared by mixing a solution of Ferric-citrate with one of Sodium-phosphate. The Iron-phosphate formed dissolves in the solution of Sodium-citrate. A scale preparation is then made by evaporating the liquid to a syrupy consistency, spreading this on glass plates, and drying. The scales contain 12 percent of metallic Iron.

Ferric-pyrophosphate (Ferri pyrophosphas), $Fe_4(P_2O_7)_3$

Insoluble in pure water, soluble in a solution of Sodium-citrate. The official form is made soluble in this manner, and is called 'soluble Iron-pyrophosphate.' It is prepared by mixing solutions of Iron-citrate and Sodium-pyrophosphate; Ferric-pyrophosphate is formed, and dissolves in the Sodium-citrate. The scale preparation is made from this. The official appears as green scales, and should contain about 10 percent of metallic Iron.

Ferric-oxide (Ferri oxidum), Fe_2O_3

A reddish-brown substance, the everyday 'rust,' formed by the exposure of Iron, and found native as an ore. It can also

be obtained by heating Ferric-hydroxide, which gives up water and forms the oxide:

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O$$

It is insoluble in water, and, after having been much heated, but slowly soluble in acids.

Test for all Iron salts: With Hydrogen-sulphide or Ammonium-sulphide in alkaline solutions, they give a black precipitate of Iron-sulphide, soluble in dilute acids.

Tests for Ferric salts only: 1, Ammonium- Potassium-, or Sodium- hydroxide gives a brown precipitate with all but the citrate and tartrate. 2, Potassium-ferrocyanide gives a blue precipitate (prussian blue). 3, Tannic acid gives a black precipitate (ink) soluble in oxalic acid. 4, Potassium-sulphocyanide gives a blood-red color.

Tests for Ferrous salts only: 1, After boiling with nitric acid, they give the previous tests. 2, With Potassium-ferricyanide they give a blue precipitate (Turnbull's blue).

COBALT and NICKEL

Co:58.56 Ni:58.3

VALENCE, II (III).

These are white metals, resembling Iron. They occur naturally as sulphides and arsenides. Nickel is much used as a coin-alloy. German silver is an alloy of Nickel, Copper and Zinc. Nickel salts are green. Cobalt salts, in moist condition, are pink; but when dry show a beautiful blue color. They are used to color glass.

Family B—the Palladium Family.

This consists of Ruthenium, Rhodium, and Palladium .Their valence is 2 and 4, and they form -ous and -ic compounds.

They are found with Platinum in the native state, and, together with Platinum, Osmium and Iridium, constitute the Platinum-metals. They are all stable and do not oxidise in air.

PALLADIUM.

SYMBOL, Pd; AT. MASS, 105.7; VALENCE, II, IV.

This resembles Platinum, but is more Silver-like. It occludes large quantities of Hydrogen (see occlusion).

Palladous-chloride, $PdCl_2$

Brown crystals, obtained by dissolving metallic Palladium in aqua regia, and evaporating the solution. Used as a test for Carbon-monoxide, which precipitates finely-powdered metallic Platinum. Also used for the quantitative determination of Iodine in iodides.

Palladous-nitrate, $Pd(NO_3)_2$

Prepared by dissolving metallic Palladium in fuming nitric acid and evaporating the solution.

Family C—the Platinum Family.

Consists of Osmium, Iridium and Platinum. They are found together in the native state. Their general valence is 2 and 4, but Osmium forms an oxide, OsO_4, showing a valence of 8.

OSMIUM.

SYMBOL, Os; AT. MASS, 189.6; VALENCE, II, IV.

This is a hard, bluish metal, not fused as yet. In finely-powdered condition, it has a peculiar, pungent odor, particularly if warmed, oxidising to Osmium-tetroxide, which causes the odor. Hence the name, which means odor. Osmium is the heaviest of metals.

Osmium-tetroxide.

Also called *osmic acid,* consists of colorless, bright needles, which, on being heated, melt and then sublime. It has a sharp odor, irritating to the respiratory apparatus. It is soluble in water, forming a colorless, neutral solution. Therefore *it is not an acid.* It is a strong oxidising agent, and decolorises indigo. It is used in microscopy as a test for organic substances, with some of which, fats especially, it gives a black precipitate.

IRIDIUM.

SYMBOL, Ir; AT. MASS, 191.5; VALENCE, II, IV.

This is a heavy, stable metal.

PLATINUM.

SYMBOL, Pt; AT. MASS, 193.3; VALENCE, II, IV.

This is a gray, heavy metal, its specific gravity being about 20. It requires an Oxy-Hydrogen flame to melt it, is not oxidised by ordinary oxidising agents, and is not affected by chemical reagents except Chlorine and nitro-hydrochloric acid. These form Platinic-chloride ($PtCl_4$). On account of its resistance to change, Platinum is much used for heating-apparatus, etc.

It is found in Russia, Brazil, Sumatra, California, in metallic form. It also occurs in minerals mixed with the 'Platinum metals.' These also resist chemical action in the same manner as Platinum. The standard weights and measures of the different governments are made of an alloy of Platinum and Iridium.

In powdered condition (Platinum-black) Platinum is an energetic katalyser. This form is obtained by treating Platinum-chloride with metallic Zinc, or boiling it with glucose and Sodium-carbonate. It is also obtained by heating dry Platinum-Ammonium-chloride.

Platinic-chloride, $PtCl_4$

A brownish, deliquescent mass, soluble in water. Prepared by dissolving metallic Platinum in nitro-hydrochloric acid. Used as a test for Ammonium, Potassium, and the alkaloids. With these substances, it gives yellow precipitates which are double salts of Platinic-chloride and the chloride of the other factor to the reaction. When the Ammonium double salt is heated, it gives up Chlorine and Ammonium-chloride, leaving the Platinum as a spongy mass (Platinum-black, Platinum-sponge).

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